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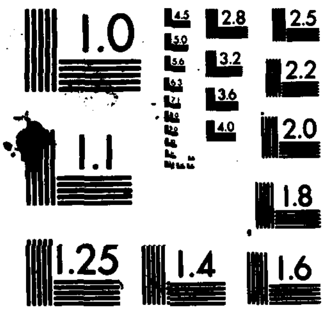

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COMPRESSIBILITY OF COLLOIDS: I. COMPRESSIBILITY STUDIES OF AQUEOUS SOLUTIONS OF AMPHIPHILIC POLYMERS AND THEIR ADSORBED STATE ON POLYSTYRENE LATEX DISPERSIONS BY ULTRASONIC VELOCITY MEASUREMENTS

by

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Sound velocity measurements were made to obtain compressibility values at 2 MHz, and to investigate the influence of the interface in dispersions of electrostatically stabilized dispersions. The measurements were made on aqueous dispersions of polystyrene latex as a function of volume concentration up to 49% and temperature up to 80°C (approaching the glass transition temperature), andin solutions of 72.5% and 78% hydrolyzed polyvinyl alcohol-polyvinyl acetate block copolymers (PVA) as a function

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of temperature above and below their cloud points. The measurements were extended to latex coated with PVA under conditions known to give a 30 nm layer at room temperature. These dispersions give a resultant compressibility lower than expected from the simple additive effect of the separate components at 25°C and higher. The decrease in compressibility may be due to either or both of two effects: the hydrophobic interaction between the acetate groups and the polymer backbone of the polystyrene latex results in a more rigid structure, and the suppression by the PVA coating of the association-dissociation reaction responsible for the remarkable high adsorption of ultrasound will result in a lower compressibility.

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INTRODUCTION

This paper presents the adiabatic compressibility of colloidal system consisting of polystyrene latex particles with and without an adsorbed layer of a block co-polymer, polyvinyl alcohol-polyvinyl acetate polymer, (PVA). the mechanical properties, surface chemistry and the compressibility of the adsorbed layers are of interest in the study of sterically stabilized colloidal dispersions. The use of ultrasonic velocity measurements in such systems is new and the following introduction provides the background knowledge.

It is customary in the thermodynamical theory of solutions that excess properties are described by comparing these properties with ideal solutions. Properties such as: partial molal volume, the chemical potential and the coefficient of isothermal compressibility are considered.

The apparent molar compressibility $\phi\kappa_2$ of a solute in a solution is defined by the following equation:

$$\phi\kappa_2 = (\beta v - n_1\beta_1\bar{v}_1^o)/n_2 \qquad (1)$$

where v is the volume of the solution containing n_1 moles of solvent and n_2 moles of solute and $\bar{v}_1^o$ is the molal volume of the pure solvent. β and β_1 are respectively the compressibility of the solution and of the pure solvent. It can be seen that if the solution is ideal the apparent molal compressibility of the solute is that of the pure substance. On the other hand, the difference between these two quantities reflects the degree of the interaction of the solute-solvent and solute-solute.

Ultrasonic velocity measurements permit the evaluation of the adiabatic compressibility of the liquid through the equation:

$$C = (\beta\rho)^{-1/2} \qquad (2)$$

where C and ρ are the velocity of sound and the density respectively.

Ultrasonic velocity measurements have been made[1-3] to determine the number of water molecules bound to the ions of an electrolyte in an aqueous solution. The assumption is made that the compressibility of primary water of hydration and the ion itself are both negligibly small in comparison with the "free" water. However, the above assumption is not valid for the aqueous solution of non-ionic molecules and polymers where the strong electrostriction of an ion on the molecules does not exist.

In aqueous solutions of such molecules and polymers the compressibility of the water molecules structured around the hydrophilic segments of polymers will be comparable to the compressibility of "free" water in the bulk of the solution. This was first pointed out by Shiio and his co-workers.[4] They also show that for low molecular weight solutes such as sugars, the compressibility of the solute molecules is near zero in experiments in which the bound water is displaced by ethyl alcohol. High molecular weight polymers, however, cannot be considered incompressible. Recently Shiio's model for adiabatic compressibility of polymers was applied to the concentration dependence of ultrasonic velocity of solutions of nucleic acid bases and their derivatives,[5] to determine the effect of the hydration layer.

Compressibility of a solid can be determined by measuring the velocity of sound waves in a dispersion of finely divided solid in a liquid. The earliest theoretical treatment for velocity of sound waves in such dispersions was given by Wood[6] where the values of density and compressibility are simply considered as the volume average of the two components;

$$\beta_{PL} = \phi\beta_P + (1-\phi)\beta_L \qquad (3)$$

where ϕ is the volume fraction of the particles, or expressed as the bulk modulus:

$$K_{pL} = \frac{K_L K_p}{\phi K_p - (1-\phi)K_L} \tag{4}$$

and the for the density:

$$\rho = \phi\rho_p + (1-\phi)\rho_L \tag{5}$$

ρ, ρ_L *and* ρ_p are the densities of the dispersion, the liquid and the particles respectively. From equation (1) we obtain Wood's equation:

$$C = \left(\frac{1}{[\phi\beta_p + (1-\phi)\beta_L][\phi\rho_p + (1-\phi)\rho_L]}\right)^{1/2} \tag{6}$$

The assumption implicit in Wood's treatment is that the particle and medium move together. As a result, it is a reasonable formula for low frequencies, or for systems with particles of density similar to the medium (such as polymer colloids). The deviation from Wood's formula e.g., (6), can result from the presence of the following effects:

(i) Relative motion: the particle and the medium do not move together in the sound field unless their densities are the same. The result of relative motion is to increase velocity.[7-9]

(ii) Skeleton effect: in the concentrated dispersion of structure forming particles, (e.g., card house structure in clays) water or electrolyte within the skeleton does "circulate" under the influence of the incidence sound wave. The extent of the "circulation" in this fluid saturated skeleton frame basically depends on the permeability and the pore size parameters. Although various theories[10-12] are published to describe the fundamentals of the sound propagation in concentrated dispersions, their successful applications to the experiments depends on the careful selection of the various parameters which are very difficult to measure independently. The nature of the forces causing this skeleton frame are not discussed. Recently, work done[13] in our laboratory showed that the forces causing the card house structure of the skeleton frame are electrostatic in origin.

(iii) Hydration layer effect: The restructuring of water occurs in a hydration layer at the solid-liquid interface (for oxides and inorganic colloids) and polymer end groups - liquid interface (for polymer colloids). It was shown[14] that similar to the structured water around the ions, hydration layers around colloidal silica particles are less compressible then the free water.

(iv) The effect of the surface chemical reactions on ultrasonic velocity and compressibility. The uncompensated volume change associated with a chemical reaction may give rise to an additional contribution to the compressibility, and hence a decrease in velocity as well as an increase in absorption.

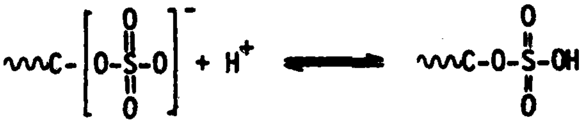
It was shown in an earlier work of two of the present authors[15] that ultrasonic absorption in electrostatically stabilized dispersions of carefully cleaned colloidal particles is strongly influenced by the nature of the electrolyte-particle interface. The colloidal particles dressed with sulfonate functional end groups in addition to sulfate end groups (surace sites) showed very high absorption, particularly in the presence of as little as 10^{-5} M 2:1 electrolyte, over and above that of classic loss mechanisms for such dispersions (heat conduction and viscous drag losses). Unlike the latex bearing sulfonate end groups, the particles containing only sulfate end groups exhibit generally lower absorption, but nevertheless higher than expected from classic losses. An adsorbed layer of a block co-polymer (PVA) on the particle surface of the former type decreased the excess absorption by as much as three orders of magnitude.

It was concluded that association-dissociation of the colloid and the counter-ion as a single step, chemical relaxation mechanism produced absorption, and that for sulfonate bearing latices this was particularly active under the conditions and frequencies used (3-30 MHz).

The insensitivity of the excess absorption to the pH in the dilute dispersions of the sulfate end-group bearing latices suggests that the relaxation process cannot be attributed to the hydrolysis process:

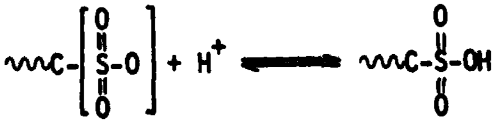
$$\sim\!\sim C-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH + H_2O \rightleftharpoons \sim\!\sim OH + HSO_4^- + H^+ \qquad (7)$$

However, the excess sound absorption can be attributed to the association-dissociation process:



$$\sim\!\sim C-\left[O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O\right]^- + H^+ \rightleftharpoons \sim\!\sim C-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \qquad (8)$$

when involving the sulfate end-groups, and



$$\sim\!\sim C-\left[\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O\right] + H^+ \rightleftharpoons \sim\!\sim C-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \qquad (9)$$

when involving the sulfonate end-groups.

The ultrasonic absorption in the carefully cleaned polystyrene particle dispersions bearing sulfonate end-groups exhibit a maximum absorption per wavelength around 3 MHz.[15] Unpublished absorption measurements done at Case laboratory on polystyrene latex particles prepared with dispersion polymerization of styrene with styrene sulfonic acid as ionic co-monomer over the frequency range 10 to 250 MHz for three particle sizes also indicated a relaxation frequency below 10 MHz.

The frequency dependence of excess absorption in dilute dispersions of these latices can be compared with the estimated relaxation in sulfurous and sulfuric acid. For sulfurous acid it has been shown[16] that the chemical equilibrium given in eq. (10) or perhaps one step in that reaction was the cause of the measured excess absorption:

$$H_2O + SO_2 \rightleftharpoons H^+ + HSO_3^- \tag{10}$$

and the calculated relaxation times for this equilibrium correspond to a relaxation frequency around 2 MHz for a conc. of 0.054 M. As one can see, although the reactions are not the same, the relaxation frequency is quite similar.

Unlike the sulfonate bearing latices, the sulfate bearing latices showed continuous increase of excess absorption per wavelength at $(\alpha\lambda)_r$ with increasing frequency up to 30 MHz without any indication of a nearby relaxation. Measurements were not available above 30 MHz. The measured excess absorption[26] in sulfuric acid has been attributed to the reaction

$$H^+ + SO_4^{--} \rightleftharpoons HSO_4^- \tag{11}$$

and the calculated relaxation times for this equilibrium correspond to the relaxation frequencies of 400-500 MHz for concentrations of 0.005 and 0.01 M.

Unfortunately, the frequency range that could be reached in the earlier study was limited to above 3 MHz. Data at and below the relaxation frequency are lacking at present. Furthermore, the reliability of the results dees below 10 MHz with measurements done with the pulse-echo technique. are no data on colloids in the literature with which to compare the ts concerning the specific interaction of the particles with counter-

he adiabatic compressibility of the system under study will contain ll dispersive contribution B'_r associated with the relaxation process an be written as the sum of the two terms

$$\beta = \beta'_r + \beta_\infty \qquad (12)$$

e β_∞ is the instantaneous compressibility. The variation of β'_r with uency is given by

$$\beta'_r = \frac{\beta_r}{1 + i\omega\tau} \qquad (13)$$

constant β_r associated with the relaxation adiabatic compressibility iven:[17]

$$\beta_r = -\frac{1}{V}\left[\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S\right] \qquad (14)$$

partial derivatives of the volume changes under constant temperature the pressure in eq. (12) are due to the shift of the chemical equilibrium reactions (8) and (9), while the volumes of the other components remain tant. This compressibility is one of the contributors of the total comsibility measured in this work and the major contributor of the "surface- compressibility" of the uncoated polystyrene particles. In view of the l particle size and the small density difference between particles and id, the relative motion losses are expected to be small. Furthermore, ace hydration effects also should be small since the polystyrene latex icles, have hydrophobic surfaces. Therefore, the deviation from Wood's ula [eq. (6)] may be particularly due to the surface chemical reaction.

The magnitude of the relaxation compressibility can be estimated from $\alpha\lambda$ or a single relaxation time chemical reaction. β_r and $(\alpha\lambda)_r$ are related by the equation

$$(\alpha\lambda)_r = \frac{\pi\beta_r}{\beta_0} \cdot \frac{\omega\tau}{1+\omega^2\tau^2} \qquad (15)$$

where β_0 = compressibility at $\omega = 0$.

For an association-dissociation reaction equilibrium, the excess absorption per wavelength is given by the approximate equation[17]

$$(\alpha\lambda)_r = \frac{\pi(\Delta V^\circ)^2 C_0}{\beta_0 RT} \left[\frac{2-\sigma}{\sigma(1-\sigma)} + \left(\frac{\partial \ln \gamma^2}{\partial\sigma}\right)_T\right]^{-1} \cdot \frac{\omega\tau}{1+\omega^2\tau^2} \qquad (16)$$

where ΔV° is the standard state volume change of the reaction, C_0 is the concentration of the electrolyte (moles/cm^3). γ is the mean ionic activity coefficient and σ is the degree of dissociation. It can be seen that when σ approaches either unity or zero, the excess absorption approaches zero too, while $\sigma = 0.588$ gives the maximum absorption.

EXPERIMENTAL

Velocity measurements were made at 2 MHz with an ultrasonic interferometer (Schall Interferometer, type SI-2000). The driving signal was obtained from a crystal controlled oscillator. Standing waves were established between the driving transducer and the traviling reflector. The wavelength of the sound waves was determined by observing the distance of travel of the reflector between a number of successive minima of the driving current of the transducer. The interferometer was thermostated so that during the measurements the temperature was kept constant within ± 0.02°C over the entire temperature range. The velocity value obtained for pure water, after correction for small temperature variations, was $1.4975 \pm 0.0005 \times 10^5$ cms^{-1}, compared with the 1.4970×10^5 cms^{-1} value found by Greenspan and Tscheigg[18] for 25°C.

Monodisperse polystyrene latex particles were prepared with dispersion polymerization in the absence of any added surface active agent. Two different polystyrene latex dispersions were prepared and cleaned. Particle size distribution of these two samples was determined by electron microscopy. Latex A was prepared with styrene freed from the stabilizer by distillation under reduced pressure (4 - 5 mm Hg) in nitrogen. For the free radical initiator, $K_2S_2O_8$ was used. A quantity of NaCl solution was added to control the ionic strength in order to obtain the desired particle size. The polymerization was carried out in a Pyrex apparatus at a constant temperature (70 ± 1°C) with stirring. The latex particles had a diameter of 532 ± 2nm.

In the preparation of Latex B, sodium styrene sulfonate was used along with the styrene as an ionic co-monomer. Consequently the resultant particles' composition was styrene-sodium styrene sulfonate polymer. The particles were monodisperse with a mean diameter of 141 ± 3 nm. Latex A contains $\sim SO_4H$ and OH polymer end groups mainly at the particle surface. The latter is due to the partial hydrolysis of the sulfate end groups during polymerization. Latex B contains $\sim SO_3H$ end groups as well as sulfate end groups, as a result of the ionic co-monomer.

Both latices were ion-exchanged with Dowex 1 and 50 ion-exchange resins, which were cleaned according to the procedure of Vanderhoff.[19] Each ion exchange resin was subjected to 15 cleaning cycles. After ion exchange, the latex B was concentrated to 42% w/w with a rotary evaporator. We believe that there should be very little or no contamination of polyelectrolytes on latex B from ion-exchange resins because of the extensive cleaning effort put into these resins. However, during the concentration of latex B in the rotary evaporator, certain contaminants may leach out from the bulk of the latex and strongly adsorb on the surface, thus contaminating the ion-exchanged clean surface.

One may point out that latex should be steam stripped[20] and then should be subjected to the concentration procedure. Steam stripping was found to be very effective and may be the only way of removing the unreacted monomer, oligomers and reaction by-products. However, it was found that steam stripping also strongly modifies[15] the surface structure of the particles. Adsorption isotherms of Alcotex 88/10 ($M_w = 45{,}000$; degree of hydrolysis, 88%) on steam-stripped and non-steam stripped latex (cleaned by dialysis) gives 2.9 mg/m^2 and 4.3 mg/m^2 adsorbed polymer respectively at 250 ppm bulk concentration by weight. We believe that steam stripping opens up the sub-surface layer of polystyrene particles and also may produce considerable pore volume at the electrolyte-particle interface and hence alters the compressibility of the particle. Ultrasonic absorption measurements were also strongly influenced by the steam stripping.

Detailed discussions of the preparation, characterization and cleaning of polymer colloids can be found in the previously published work.[20] The glass-transition temperature, T_g, of latex A was determined with differential thermal analysis and found to be $T_g = 103°C$.

The 72% and 78% hydrolyzed PVA (Alcotex) samples were kindly donated by Dr. S. Ormondroyd, of Revertex Limited, Essex, England, and were used without further fractionation or purification. According to the manufacturer, both the PVA samples were made from the same polyvinyl acetate which has a degree of polymerization of between 500-600 as measured by gel permeation chromatography. After hydrolysis, samples have a degree of polymerization of around 350-400. This reduction, of course, is due to the removal of the hydrolysable branches. The cloud point of the 72.5% hydrolyzed PVA is 30°C and the 78% hydrolyzed sample has a cloud point around 50°C. The density of the polymer soluions as a function of polymer concentration was measured with a Mettler digital density meter, DMA 46. After two point calibration, the reproducibility of the measurements was ± 1×10^{-4} g cm^{-3}. The values for the density of the 72.5% and 78% hydrolyzed PVA were determined from the weight of polymer and volume of water using the equivalent of eq. (5) and found to be 1.252 ± 0.002 g cm^{3} for both PVA samples. The density was found to vary linearily with concentration in the range 0 to 3 g of polymer/100 cm^{3} of water.

RESULTS, DISCUSSION AND CONCLUSIONS

Figure 1 gives the velocity determined for latices A and B at a number of concentrations. The theoretical curve (solid line) is also given using eq. (6) for $\rho_{PL} = 1.053$ g cm^{-3} and compressibility 2.6×10^{-11} cm^{2}/dyne. An equally good fit would be obtained using the $\rho_{PL} = 1.047$ g cm^{-3} and compressibility 2.7×10^{-11} cm^{2}/dyne. The velocity-concentration curve of these two latices are satisfactorily represented by either of the above constants. Both compressibility values are higher than the literature value[21] of 2.16×10^{-11} cm^{2}/dyne quoted for polystyrene about which no details are reported. The density of latices prepared with dispersion polymerization have been found to vary between 1.038 and 1.055 g/cm^{3} at 25° as determined with the succrose density gradient technique[22] with the average density being 1.047 g cm^{-3}. These determinations were made on polystyrene particles in the suspension form. However, a value of density of 1.053 g cm^{-3} at 25°C has been reported by Fox and Flory.[23] The polystyrene samples used by Fox and Flory differed from that used in the present work in that they were prepared by thermal polymerization in a non-aqueous medium and, therefore, did not contain any polar end-groups. They also studied the thermal expansion coefficient and gave the following expression for the specific volume:

$$v_{PL} = 0.943 + 2.5 \times 10^{-4}\ T$$

T is in degrees Centigrade.

The uncertainty in the density of the polystyrene latices used in this work results in an error of $\pm .1 \times 10^{-11}$ cm^2/dyne, and cannot explain the discrepancies in the compressibility values determined here and in the literature.

Since the polymer end-groups are strong acids, it is to be expected that there will be a hydration sheath around the polymer end-groups with considerably lower compressibility in the bulk solvent. However, in analogy with ultrasonic velocity work done on sulfuric acid[24] the concentration involved here, 2.5×10^{-2} M, would be expected to lead to a 0.8 m s^{-1} change in the measured velocity and a corresponding change in the compressibility. Therefore, we can conclude that the contribution of the hydration sheaths around the end-groups to the compressibility is comparable with the level of experimental accuracy.

Although this effect is measurable, it would result in a decrease of compressibility and thus would not contribute an explanation to the discrepancy.

On the other hand, the surface-chemical relaxation suggested in eq (8) and eq. (9) will effectively increase the compressibility by the amount β'_r (see eq. (12)). Furthermore, the ultrasonic absorption measurements on similar latices[15] indicate that this surface-chemical relaxation mechanism could have a measurable contribution to the total compressibility of the system, and provide the data for an estimate of the magnitude of β'_r using eq. (15) and eq. (18) assuming β is a reasonable approximation for β_0.

The magnitude of excess $\alpha\lambda$ for 1% w/w of sulfonate bearing latices[15] was 5×10^{-3} nepers/wavelength at 3 MHz, and to the extent it would be checked, it appeared to be proportional to concentration. It was also apparent that the relaxational absorption was by far the predominant cause of this absorption. On the assumption that this was the peak value of $\alpha\lambda$, equation (15) gives a value of β_r of $.0068 \times 10^{-11}$ cm^2/dyne for 1% w/w latex dispersion. While it is not valid to extrapolate to 25% w/w latex, it is informative to note that such an estimate would give $\beta_r = 0.33 \times 10^{-11}$ cm^2/dyne, and therefore, can contribute a measurable addition to the observed compressibility at 2 MHz.

The extent of the relaxational $\alpha\lambda$ exceeds that for the equivalent concentration of sulfurous acid by a factor of about 50 (low frequency data are lacking for both systems at present for an adequate comparison). The enhancement is not fully understood, but the dispersion system differs from the simple acid in several ways beyond simply the attachment of a carbon chain. The negative charges are anchored to the surface of the latex, and these charged end-groups extend out from the surface an unknown distance. It is therefore possible for a portion of the counterions (i.e., hydronium ions) of the accompanying double layer to be in a position behind the end-group (i.e., nearer the surface than the end-groups). These properties can have various effects on the association-dissociation equilibrium, and may help explain the apparent enhanced effect on the surface. With the above discussion, we support a surface-electrolyte model of the following kind. Surface and subsurface regions are considered, see Fig. (2a). Evidence for a small proportion of buried end-groups comes from a comparison of titration results on the suspension of particles intact and dissolved, or after steam stripping. The counterions are in dynamic equilibrium with the end-groups. The state A is the equivalent of so-called counterion condensation or ion-binding described by Manning.[27] The states B and C represent the subsequent states where the protons are loosely bound.

As we mentioned before, an adsorbed layer of PVA had the effect of drastically reducing the excess absorption to the level of classical losses absorption (heat conduction and viscous-drag losses). This should in turn reduce the excess compressibility due to the above mentioned chemical reactions by the amount of the relaxational compressibility operative at 2 MHz assuming that other sources contributing to the compressibility remain constant.

A set of measurements on latex B with and without a coating of PVA were made over a range of temperatures from 9° to 80°C, as well as on solutions of 72.5% and 78% hydrolyzed PVA. Approximately 26% (v/v) dispersions of latex B were used, and the compressibility calculated using Wood's formula are given in Fig. 3 without the PVA coating assuming the density and thermal expansion coefficient reported by Fox and Flory[23].

The compressibilities for PVA in solution as a function of temperature were calculated with the same type of formula using the density 1.252 g/cm^3 and are given in Fig. 5. Data for repeated measurements are shown for only the 72.5% hydrated PVA. The use of eq. (3) for the PVA in solution carries a greater level of assumption concerning the lack of perturbed water structure. The significance of the calculated β is thus analogous to apparent molar compressibility of ions.

In analysing the data for PVA coated latex, it became clear that the total compressibility was significantly different from that expected from the measurements of the separate components. There are two possible explanations for this finding:

(i) In the first explanation, the compressibility of the latex is assumed to remain unchanged when the PVA polymer is attached to the latex. The non-additivity of the total compressibility is then attributed to structural changes in the PVA when present as a coating on latex. In Fig. 5 the points represent the compressibility of the adsorbed PVA calculated with this assumption from the experimental velocity data. The points for the compressibility of the PVA in the coating were calculated with the equation

$$C = 1/[(\phi_L \rho_L + \phi_p \rho_p + \phi_{PVA} \rho_{PVA})(\phi_L \beta_L + \phi_p \beta_p + \phi_{PVA} \beta_{PVA})]^{\frac{1}{2}} \qquad (17)$$

Also shown is the line representing the compressibility of PVA in solution from

Fig. 4. It can be seen that in all three experiments (done with separate samples from the same stock dispersion) the compressibility lies below that for PVA in solution with the possible exception of 4°C. This may be explained on the basis that the PVA is strongly adsorbed on the polystyrene latex particles with their acetate segments anchored to the surface (with the hydrophilic segments extending out from the surface (see Fig. 2b)) and hence increases the rigidity of the polymer.

(ii) In the second explanation, the assumption is made that the compressibility of PVA in the adsorbed state is the same as in solution, i.e., no structural changes occur on adsorption. However, the adsorbed PVA hinders the surface chemical reaction between the surface sites (sulfate and sulfonate end-groups) and counterions (H^+) due to dipole-ion interactions between alcohol segments of the PVA and the end-groups of the latex. Ottewill and Vincent[25] made a study of adsorption and wetting behavior of n-alkanols of polystyrene latex particles. From the adsorption isotherm of n-butanol on the latex particles, they reached the conclusion that the interaction occurred between hydroxyl groups on the butanol molecule and the hydrophilic sites of the surface. They also concluded that adsorption of alcohol molecules on the charged hydrophilic sites leads to desorption of the counterions from the inner part of the double layer.

In Fig. 6, the solid line represents the compressibility of the latex (from Fig. 3) while the points are the compressibility calculated from data with the PVA coated latex assuming that the compressibility observed is of the right order of magnitude to be explained by the elimination of the relaxation compressibility arising from the surface chemical reaction.

With the present experimental evidence, it is not possible to distinguish between the two possible explanations give above.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. C.A. Younq who carried out the adsorption isotherms of various PVA samples on polystyrene latex samples, to Mr. M.J. Castle and Dr. M.C. Wilkinson of Chemical Defense Establishment, Porton Down, Salisbury, Wiltshire, England, for determination of the glass transition temperature of the latex A and sucrose density centrifuge density measurements on various latices. Latex A was prepared by one of the authors (M.E.G.) in Bristol University during his doctorate work. A sample of this latex used in the present work with the kind permission of Prof. D.H. Everett. This research has been supported by the Office of Naval Research.

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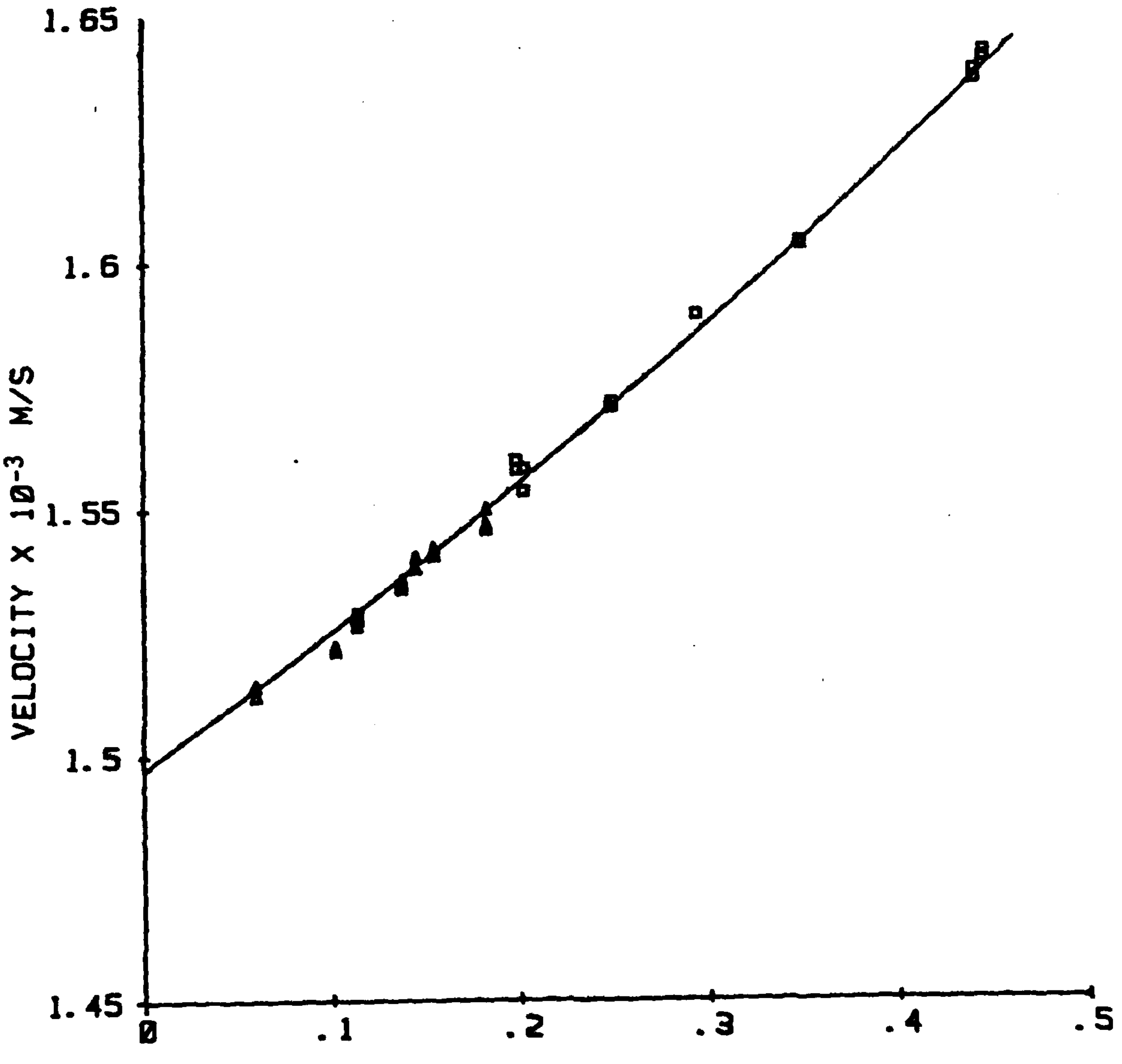


FIG. 1. Ultrasonic velocity of latex A (Δ) and latex B (□) as a function of volume fraction at 25°C. The solid line is the theoretical curve using eq. (6) for ρ_{PL} = 1.053 g cm^{-3} and compressibility 2.6 x 10^{-11} cm^2/dyne. The measurements represented in all the figures were done at 2 MHz.

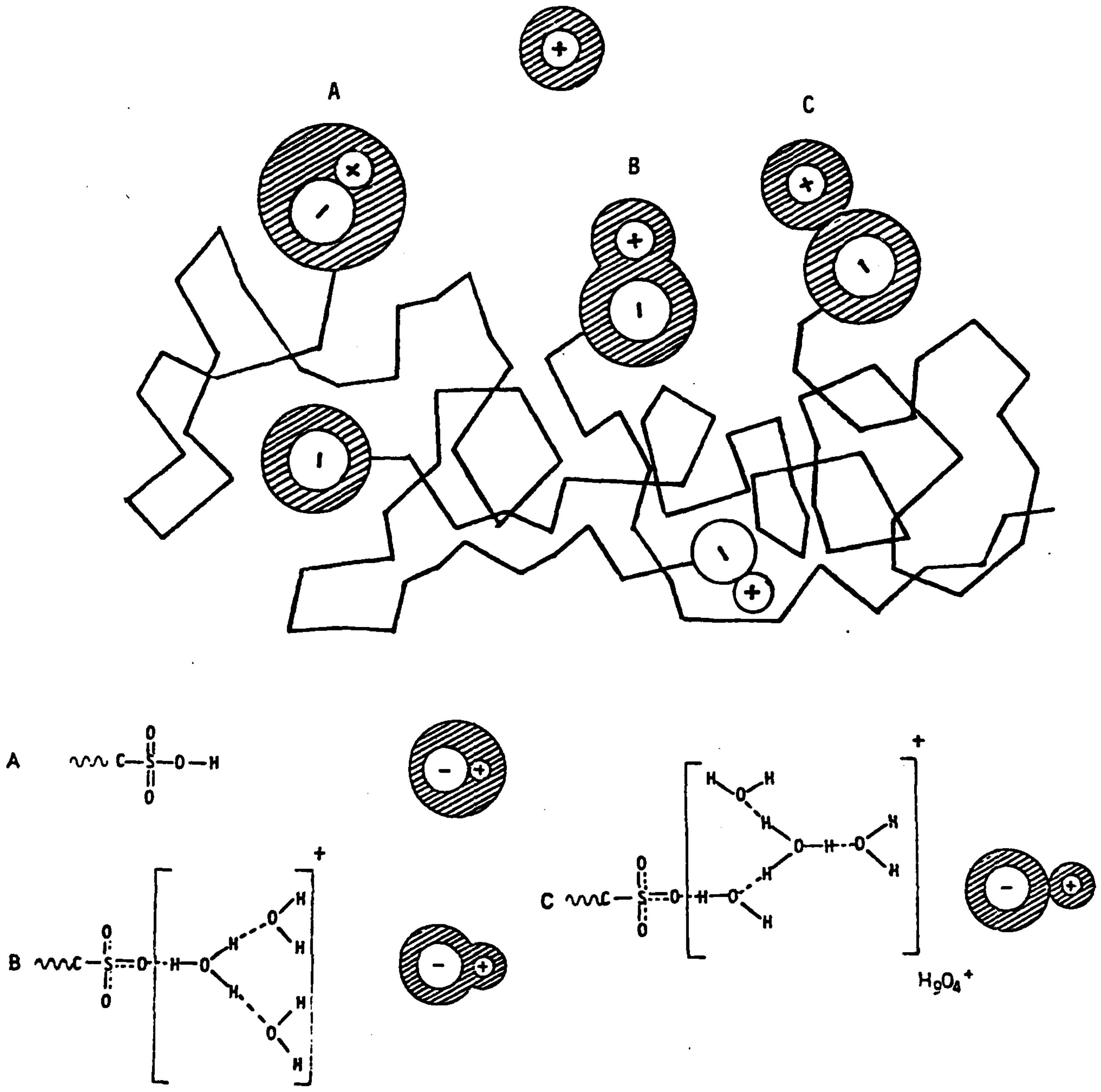
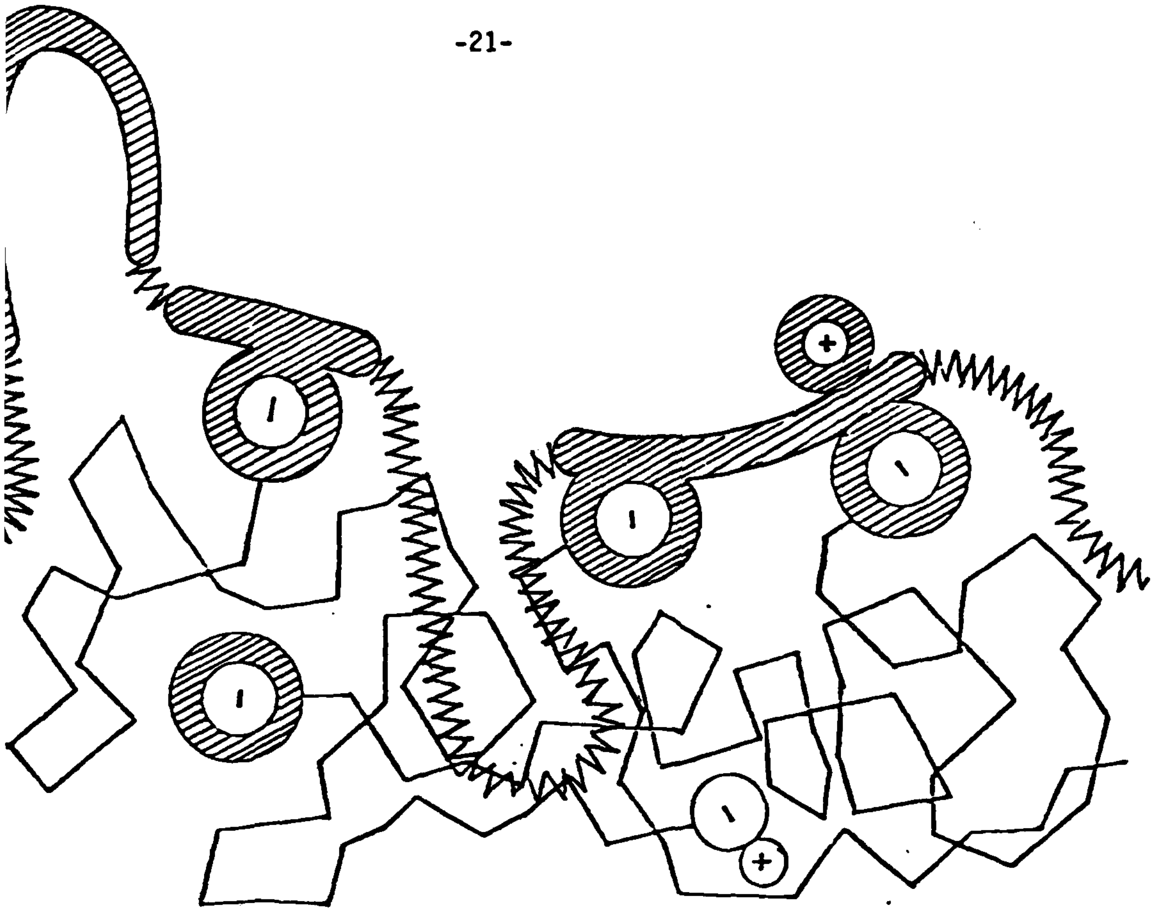


FIG. 2a. A possible model for a polymer colloid/electrolyte interface showing three states of counter-ion/polymer end group association.



2b. Model of the latex surface with a coating of PVA. The shaded segments of the PVA represent the polyvinyl alcohol parts surrounded by a hydration sheath, while the zig-zag segments represent polyvinyl acetate.

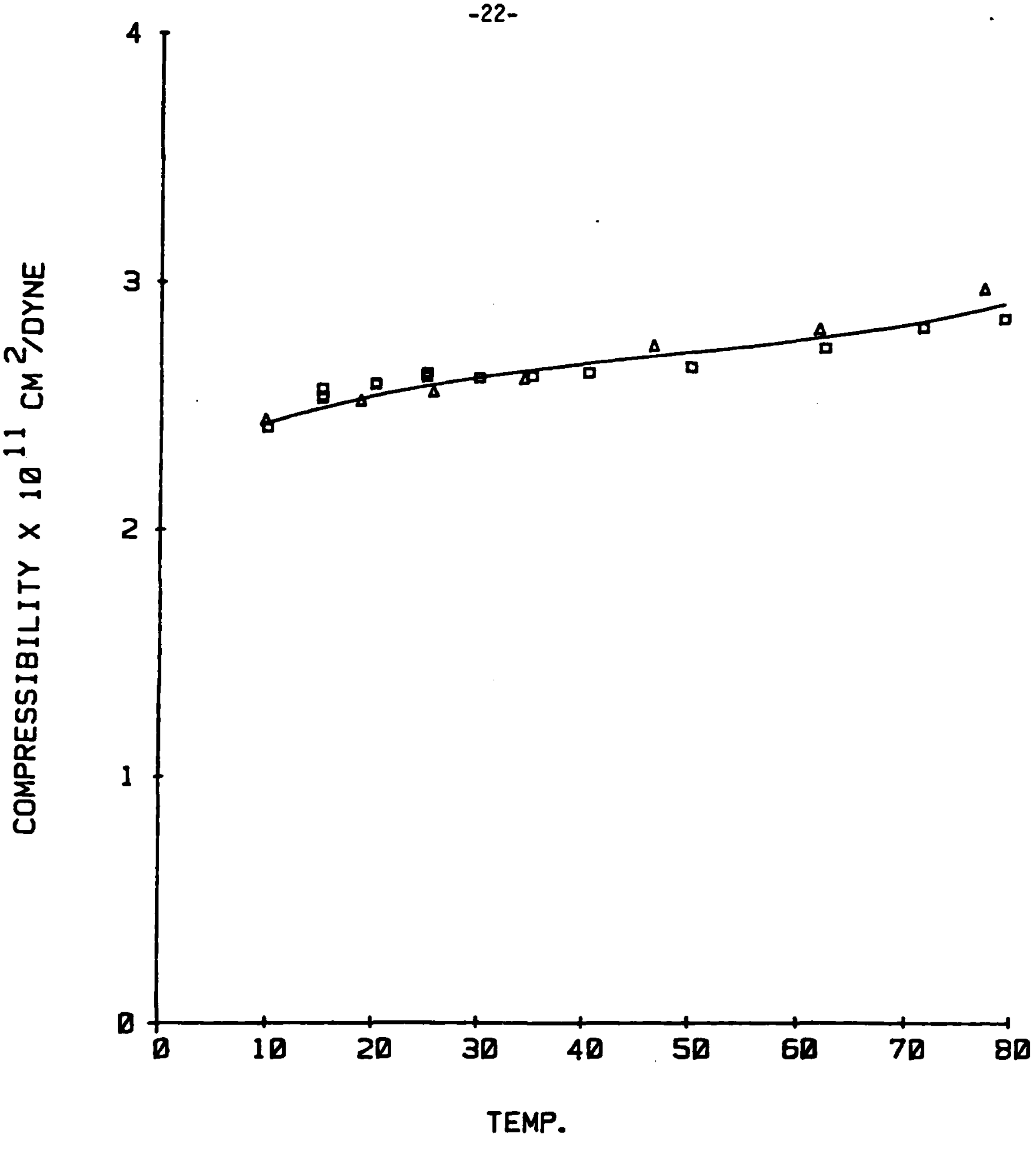


FIG. 3. Compressibility of latex B with temperature determined at a volume fraction of 26% v/v; experiments on two samples.

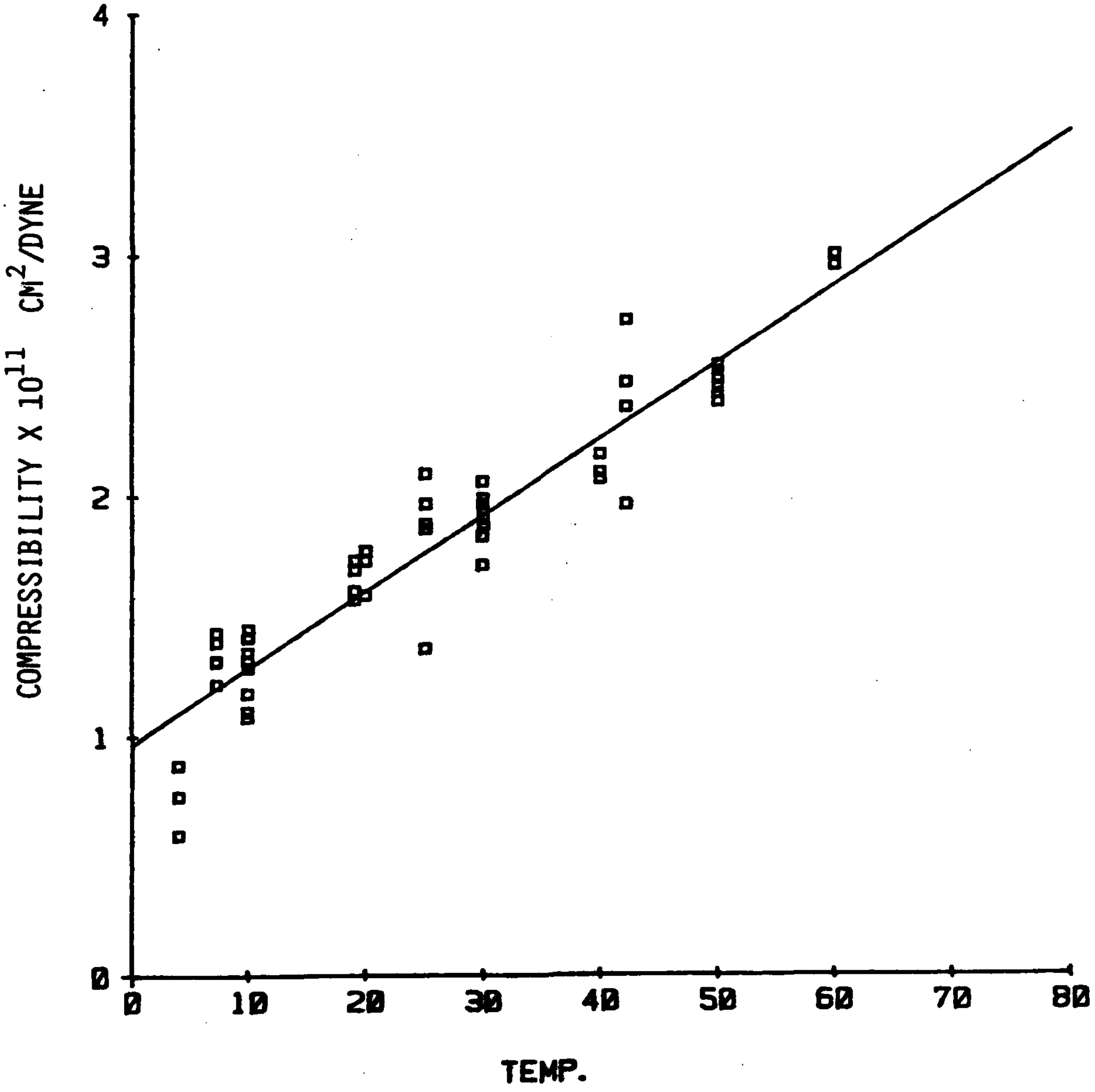


FIG. 4. The compressibility of the 72.5% hydrolyzed PVA calculated from the overall compressibility of 3.44% (by weight) aqueous solution.

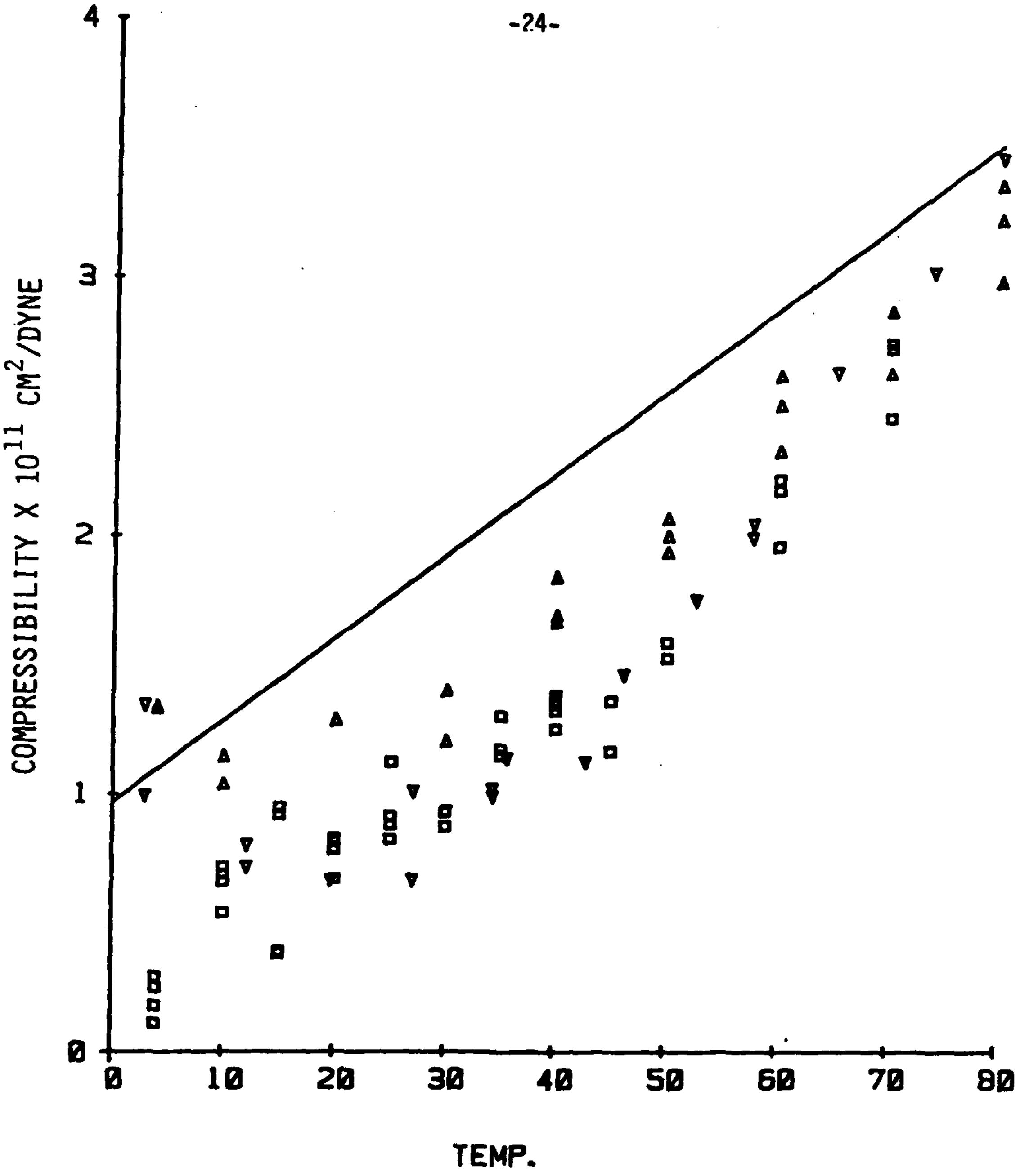


FIG. 5. The points represent the compressibility of PVA adsorbed on polystyrene latex particles on the assumption that the compressibility of other constituents are unaltered (particles and medium). The solid line represents the compressibility of the PVA in solution (see Fig. 3) and the points represent three independent experimental determinations. The volume fraction of the latex dispersions are around 26% v/v. The concentration of adsorbed PVA 2.9 mg/m^2 at 250 ppm bulk concentration.

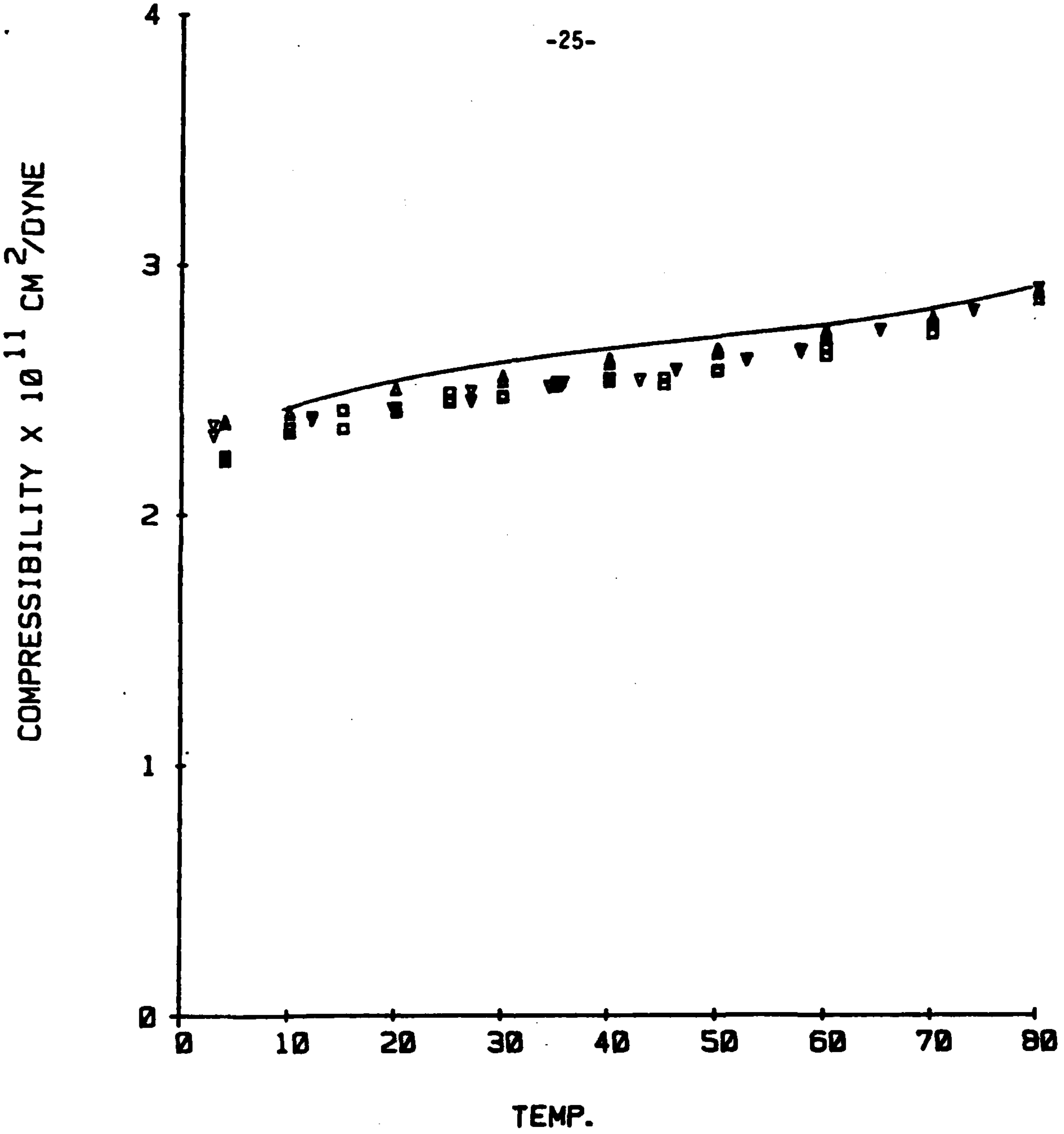


FIG. 6. The compressibility of 26% v/v polystyrene latex covered with 72.5% (□) and (Δ), 78% (∇) hydrolyzed PVA with temperature. The solid line shows the compressibility determined with uncoated latex, i.e., see Fig. 2. The is made here that the compressibility of PVA as a coating is the same as in solution.

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