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Densities, Viscosities, Speeds of Sound, and Water Solubilities of Some Polypropylene Glycol Ether Derivatives in the Temperature Range 273.15–323.15 K

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A series of end-capped polyalkylene glycols (PAG) (*n*-butyl,*n*-alkyl-substituted polypropylene glycols) and polypropylene glycols (PPG) (dialkyl-, dihalo-, bis(fluoroalkyl)-substituted polypropylene glycols) were synthesized. Optimum reaction conditions were determined with regard to time, temperature, reaction ratios, and solvents for each of the PAG and PPG derivatives. An investigation was carried out to find their suitability as potentially new sonar transducer fill fluids. The density, viscosity, and speed of sound were measured as a function of temperature, and their solubilities in water were measured for several of these derivatives. The desirable properties of some of these compounds make them potentially important transducer fill fluids.

Introduction

In spite of its several drawbacks, castor oil is still one of the most abundantly used fill fluids for sonar transducers in naval applications. However, the high viscosity and difficulty in degassing castor oil present a problem in the filling of transducers during manufacture and routine maintenance. In addition, at low temperatures and high pressures, castor oil becomes extremely viscous, which leads to a decreased acoustic response of the transducer at low frequencies. Because of this, the polyalkylene glycol, PAG, a mono-*n*-butyl-terminated polyether prepared from 1,2-propylene oxide, has been proposed as a substitute (*1*). PAG has a much lower viscosity than castor oil and exhibits a speed of sound value that closely matches that of sea water, but it has an unacceptably high water solubility. At 298.15 K, PAG dissolves 1.8% water by mass. The presence of water in the fluid degrades the electrical resistivity and changes the acoustic and pressure–volume–temperature properties. The most critical problem due to water solubility occurs when the temperature drops. The water dissolved in PAG separates, coats the interior surface of the transducer, and creates the potential hazard for short circuiting, thereby leading to failure of the transducer. Nevertheless, there is an interest in continuing the study on PAG systems because of their overall favorable characteristics, their low cost, and their low toxicity.

In the present paper, a variety of new, potential transducer fill fluids which are based on PAG- or PPG-related (disubstituted polypropylene glycols) moieties have been synthesized. The present work is oriented toward modifying the molecular structure of PAG by end-capping the hydroxyl group with an alkyl group to decrease the water solubility of the compound. The density, ρ, viscosity, η, speed of sound, u, and water solubility, s, for these compounds have been measured in the temperature interval of 273.15–323.15 K. The desirable properties possessed by some of these derivative liquids make them of potential value in their use as transducer fill fluids. A surprisingly small amount of high-quality data has been published (*2–4*) on the thermodynamic and transport properties of the mixtures of polyethylene glycol, but to the best of our knowledge, no such results on PPG and PEG derivatives have been published hitherto in the literature.

Experimental Section

Chemicals and Synthesis of Compounds. The PAG used as a starting material was obtained from Union Carbide; it had an average molecular weight of 600 with a purity of >99.5 mol %, and its structure was $C_4H_9[OCH(CH_3)CH_2]_nOH$, where n = 9 or 10. The PPG starting material was purchased from Aldrich; it had an average molecular weight of 725, and its structure was $H[OCH(CH_3)CH_2]_nOH$, where n = 12 or 13. Due to similarities in the structure of the polymeric starting materials and products and the nature of the chemical modifications of the starting material, the primary instrument used to qualitatively determine the occurrence of a reaction was an infrared spectrometer. If the starting material contained a hydroxyl group (the modification target), a decrease in intensity or complete absence of the O–H stretch band at 3460 cm^{-1} indicated the reaction occurred. In cases where the starting material did not contain a hydroxyl group, the reaction product was sent for elemental analysis to determine if a reaction occurred. When appropriate, NMR was used to determine if a reaction occurred.

End-capping of PPG or PAG with straight-chain alkyl groups provided a high percent yield of the product and presented no problems except that all of the reactions required two or three passes to achieve 100% conversion of starting material. Use of excess base and alkyl halide had no effect on the number of passes required. Because the reaction conditions involved a two-phase system, initially a phase-transfer catalyst (tetrabutylammonium hydrogen sulfate) was used in order to promote the reaction (*5, 6*). However, since polyglycols are known to function as phase-transfer catalysts (*7*), reactions were also run in the absence of tetrabutylammonium hydrogen sulfate. The latter conditions resulted in a considerably simpler workup, and in addition, infrared analysis indicated no difference in the extent of reaction. Therefore, all subsequent reactions were run without added phase-transfer catalyst.

Diethyl-end-capped PPG was synthesized in an aqueous two-phase system and in an anhydrous one-phase system to investigate the extent of reaction. No difference was observed. Both runs had to be repeated twice in order to achieve complete conversion of the starting material.

Synthesis of several branched-alkyl-end-capped PPG compounds was attempted. Thus, in this series, the end-capped compounds prepared were di-*n*-butyl-end-capped PAG, dimethyl-end-capped PPG, diethyl-end-capped PPG, and di-

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n-propyl-end-capped PPG. Also prepared was the dichloro-end-capped PPG using triphenylphosphine and carbon tetrahalide. Infrared analysis indicated end-capping of PPG with chlorine occurred as reflected in the absence of the O–H stretch band at 3460 cm^{-1}. However, the IR spectrum of dichloro-end-capped PPG showed a sharp, characteristic C–Cl stretch at 688 cm^{-1}. The presence of chlorine in the compound was further confirmed by combustion analysis.

Measurements. Density values of the compounds were measured using a 100 cm^3 capacity graduated Cassia flask which had previously been calibrated with boiled deionized water. The clean, dry Cassia flask was first weighed empty, then filled with approximately 102 cm^3 of sample, and weighed again. The difference in these two masses was the sample mass.

The flask was placed in a Neslab Endocal refrigerated circulating bath (model RTE-8) for 30 min to equilibrate. The flask was then removed and dried and a volume measurement taken. After the measurement was taken, the bath temperature was increased by 3–5 K and the flask returned to the bath to equilibrate at the new set temperature. This procedure was repeated over the desired temperature range.

All density measurements reported only at 298.15 K were made using a 2 or 25 cm^3 pycnometer depending upon the sample size. These pycnometers were calibrated using boiled deionized water. The clean, dry pycnometer was weighed empty, then filled with sample, placed in a Lauda/Brinkmann RC20 series (model T-2) refrigerated circulating bath, and allowed to equilibrate for 30 min. After 30 min, the pycnometer was rinsed with acetone to remove excess sample from the outside glass surface, then dried, and weighed. The difference in mass was the sample mass at 298.15 K. Density values were calculated as

$$\rho = \frac{\text{mass of sample (g)}}{\text{mass of pycnometer (cm}^3\text{)}} \qquad (1)$$

The speed of sound as a function of temperature was measured with a Mapco Nusonics sonic solution monitor (model 6105). A 100 cm^3 beaker was filled with approximately 80 cm^3 of sample, and the probe connected to the sonic solution monitor was immersed in the sample fluid. A paraffin film was wrapped around the top of the beaker and the probe to seal out any water which could contaminate the sample from the temperature bath. The beaker was then placed in a Neslab Endocal refrigerated circulating bath (model RTE-8) for 30 min to equilibrate, and then an output frequency value was recorded from a Hewlett-Packard electronic counter (model 5512A). The circulating bath temperature was then raised by 3–5 K and the fluid allowed to equilibrate at the new set temperature. This procedure was repeated over the desired temperature range.

An acoustic pulse of 1.8 MHz was transmitted through the fluid from a transmitting transducer at the top of the probe to a reflector at the bottom of the probe. The receiving transducer then initiated a second pulse from the transmitting transducer to repeat the cycle. This cycling continued at a rate limited by the reaction time of the electronics and the pulse transit time through the fluid. The output frequency of this continuous cycling is directly related to the speed of sound, u, of the fluid which is calculated as

$$u = \frac{l(1 + \alpha T)}{7 - (AF \times 10^{-6})} \qquad (2)$$

where l is the sound path length, α is the coefficient of thermal expansion of the probe, T is the fluid temperature, A is the electronic time delay, and F is the output frequency. The factor 7 is used for a greater resolution.

The viscosity was measured with a Brookfield Rheolog viscometer. This rotational viscometer measures the torque required to rotate an element in a liquid and relates this torque to viscosity. The signal output is converted to viscosity units.

The viscometer was previously calibrated with standard oils of known viscosity over the temperature range of 273.15–323.15 K. An 8 cm^3 portion of the sample to be measured was pipetted into the stainless steel sample holder, stoppered, and placed in a Neslab Endocal refrigerated circulating bath (model RTE-8) for 30 min to equilibrate. At the end of 30 min, the sample holder was removed, dried, and placed in the insulated sample holder stand. The spindle of the viscometer was then aligned with the sample holder stand and lowered into the sample holder. In order to allow for steady, reproducible revolutions per every minute of the spindle, measurements were taken at 60 rpm with a 2-min equilibrium time period from the time the spindle began rotating to the time the measurement was taken. After the measurement was taken, the circulating bath was increased by 3–5 K, and the sample holder stoppered and placed back in the bath to equilibrate to the newly set temperature. This procedure was repeated over the desired temperature range. The viscosity was calculated from eq 3. The value of the spindle factor taken for calculation was 125.

$$\eta = \text{(output value)} \times \text{(chart expansion)} \times \text{(spindle factor)} \qquad (3)$$

The solubility of water in end-capped PPG or PAG samples was determined by Dean-Stark azeotropic distillation and/or Karl-Fischer titration. The procedure for a Dean-Stark azeotropic distillation is as follows: a known mass (approximately 25 g) of the dry sample was pipetted into a 250 cm^3 single-necked, round-bottomed flask followed by a known volume of the deionized water equal to 2% of the mass of the sample. Stirring or agitation was prohibited as this would cause emulsion formation due to the close density values of the sample and water. The water/sample solution was allowed to set for 24 h, and the excess water which did not dissolve in the sample was removed with a Pasteur pipet. A 100 cm^3 portion of the previously dried (molecular sieves) hexane was added to the sample, and a Dean-Stark moisture trap (with cubic centimeter subdivisions), attached to a condenser fitted with a drying tube, was then connected to the sample flask. The sample was heated to reflux for 24 h, then the volume of water in the trap was measured, and the percent water was calculated:

$$\%\ H_2O = \frac{\text{mass of water}}{\text{mass of sample}} \qquad (4)$$

The procedure for determining water solubility in end-capped PPG or PAG samples using Karl-Fischer titration is described as follows: a known mass (approximately 10–20 g) of the dry sample was pipetted into a 50 cm^3 Erlenmeyer flask. A known volume of deionized water equal to 2% of the mass of the sample was pipetted into the sample. The water/sample solution was allowed to set generally for 38 h to achieve equilibrium unless otherwise mentioned in Table 1. The insoluble excess in the sample was removed with a Pasteur pipet.

The titrations were performed using a Fischer Scientific K-F titrator (model 390/392). Standardization was done with known masses of deionized water. Known mass samples (approximately 2–3 g) were titrated to an end point. These titrations were repeated at least twice and in most cases in

Table 1. Water Solubility *s* of various end-capped PAG/PPG Derivatives at 298.15 K

compound	s/(mass %) Dean-Stark	s/(mass %) Karl-Fischer
(I) di-*n*-butyl-end-capped PAG	0.62	1.218
(II) *n*-butyl, methyl-end-capped PAG	0.76	1.325
(III) dimethyl-end-capped PPG	1.04	1.866
(IV) diethyl-end-capped PPG	1.03	1.897
(V) di-*n*-propyl-end-capped PPG	0.38	1.439
(VI) dichloro-end-capped PPG		0.938[a]
(VII) bis(2,2,2-trifluoroethyl)-end-capped PPG	0.45	
PAG[b]		1.800
PPG	*c*	*c*

[a] Water/sample stood for 24 h. [b] Reference 1. [c] Soluble in all proportions.

triplicate. The percent water was calculated from the following relationship:

$$\text{titer} = \frac{\text{mg of water}}{\text{cm}^3 \text{ of Fischer reagent}} \tag{5}$$

Titer is determined from standardization with deionized water as

$$\% \ H_2O = \frac{(\text{titer}) \times (\text{cm}^3 \text{ of Fischer reagent}) \times 100}{\text{mg of sample}} \tag{6}$$

Other instruments and analytical services used in the analyses were as follows: Perkin-Elmer 457 grating infrared spectrometer, Nicolet MX-S Fourier transform infrared spectrophotometer, and Varian EM-360A 60-MHz nuclear magnetic resonance spectrometer. Elemental analyses were performed by Robertson Laboratory, Florham Park, NJ 07932.

Results and Discussion

Our major goal was to discover a suitable substitute for castor oil which has a high viscosity and can form intermolecular hydrogen bonds readily with other compounds (*8*). The nearly 13-fold decrease in viscosity of PAG, a mono-end-capped PPG, as compared to castor oil is attributed to a decrease in intermolecular hydrogen-bonding through its hydroxy group. However, end-capping the hydroxy group of PPG with straight-chain alkanes decreased the viscosity at 298.15 K by a factor of 17–22. It appears that end-capping the polyalkylene glycols essentially eliminates intermolecular hydrogen-bonding.

The change in viscosity as a function of temperature is given in Figure 1. It is observed that, for dichloro-end-capped PPG, viscosity values are higher than for all the remaining compounds and there is a steep decrease in viscosity values from 273.15 to about 298.15 K. On the other hand, for water, the viscosity as a function of temperature decreases within a narrow range. The values of viscosities for the remaining compounds are intermediary to those of water and dichloro-end-capped PPG. This might be due to the fact that the intermolecular hydrogen-bonding which is present in PAG and polar bonding attraction which occurs in dichloro-end-capped PPG due to the electronegativity of chlorine atoms are absent in the straight-chain-alkane-end-capped PPGs. The attractive forces appear to increase the viscosity as a function of temperature although the helical conformation of the molecules tends to moderate the increase in viscosity as observed (*9*).

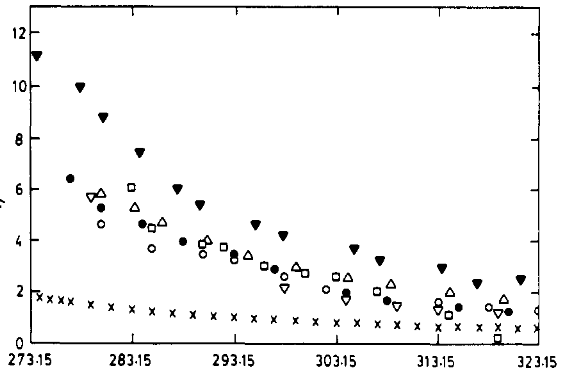

Figure 1. Dependence of viscosity on temperature for various end-capped PAG/PPG derivatives. Symbols: (×) water; (●) dimethyl-end-capped PPG; (□) diethyl-end-capped PPG; (▽) *n*-butyl,methyl-end-capped PAG; (○) di-*n*-butyl-end-capped PAG; (△) di-*n*-propyl-end-capped PPG; (▼) dichloro-end-capped PPG.

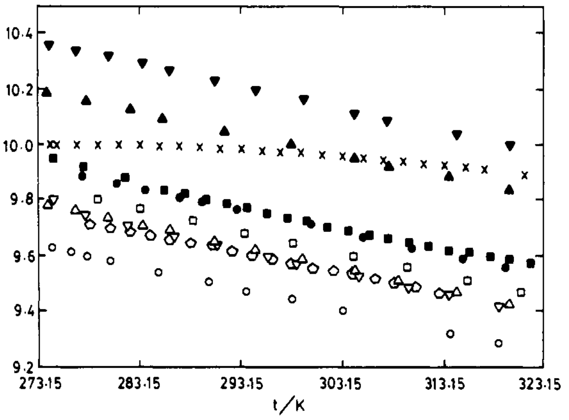

Figure 2. Dependence of density on temperature for various end-capped PAG/PPG derivatives. Symbols: (×) water; (✪) castor oil; (■) PAG; (△) PPG; (●) dimethyl-end-capped PPG; (□) diethyl-end-capped PPG; (▽) *n*-butyl,methyl-end-capped PAG; (○) di-*n*-butyl-end-capped PAG; (△) di-*n*-propyl-end-capped PPG; (▼) dichloro-end-capped PPG.

As regards density results, a linear relationship exists between density and temperature for end-capped PAG/PPG derivatives as shown in Figure 2. On the basis of the small differences in slope for alkane-end-capped PPG/PAG derivatives, it is observed that the change in density as a function of temperature depends on the propylene ether backbone structure. PAG and PPG have higher densities than their straight-chain-hydrocarbon-alkane-end-capped derivatives due to the terminal hydroxy groups which undergo intermolecular hydrogen-bonding, thus increasing the packing of molecules per unit volume. When the hydroxyl group is replaced by a straight-chain alkoxy group, the density decreases because hydrogen-bonding is eliminated and the close packing is absent. In proceeding from a methyl to an *n*-butyl end-capping group, the mass of the capping group increases, but density decreases. This is probably due to the increased disruption of the packing of the molecules due to the bulkiness of the group as the carbon number increases. This effect was not seen in the case of dichloro-end-capped PPG, which contains one or two isopropyl-end-capped groups, as the density is greater than those of diethyl- or di-*n*-propyl-end-capped derivatives.

However, from the results presented there appears to be a correlation between the size and mass of the capping group and density. For instance, replacing the three hydrogens in the ethyl capping with three fluorine atoms increased the

Table 2. Estimated Coefficients of the Equation for Viscosity, η, and Density, ρ, of Various End-Capped PAG/PPG Derivatives

	η/(mPa·s)			ρ/(kg·m^{-3})		
compound[a]	a	$-b$	r	a	$-b$	r
I	0.742	0.013	0.983	963.1	0.768	0.999
II	0.815	0.017	0.960	977.4	0.787	0.999
III	0.851	0.017	0.993	991.4	0.786	0.999
IV	0.949	0.020	0.951	983.4	0.742	0.982
V	0.844	0.014	0.991	978.2	0.774	0.999
VI	1.023	0.014	0.972	1037	0.801	0.801
PAG[b]	2.278	0.022		996.2	1.100	
PPG				1019	0.774	0.999
castor oil[c]	3.717	0.035				

[a] Numbers I–VI refer to the same compounds as given in Table 1. [b] Reference 1. [c] Reference 10.

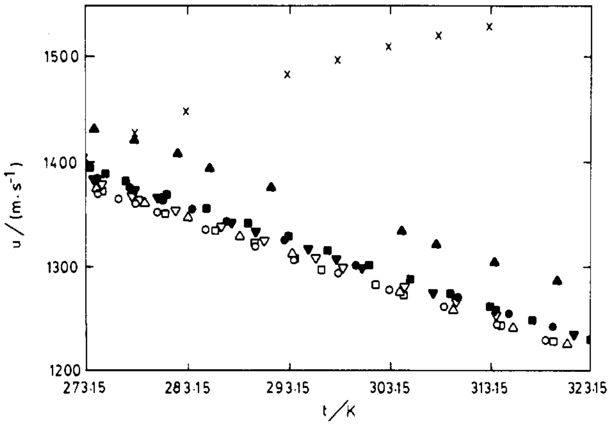

Figure 3. Dependence of the speed of sound on temperature for various end-capped PAG/PPG derivatives. Symbols are the same as given in Figure 1.

density as expected due to the added mass of fluorine atoms. When the hydroxyl group was replaced with a halogen atom, the difluoro-end-capped PPG exhibited a higher density than the dichloro-end-capped PPG. This behavior suggests that the size of the group overrides its mass for increasing the density.

A linear regression analysis of the viscosity and density values was attempted to estimate the coefficients, a and b, of eq 7.

$$\ln(\rho \text{ or } \eta) = a + b(T/\mathrm{K}) \qquad (7)$$

The correlation coefficient values, r, and the estimated values of a and b are given in Table 2.

As shown in Figure 3, a linear relationship exists between the speed of sound and temperature for the end-capped PPG/PAG derivatives. For the polypropylene glycol derivatives, the slope of the lines are very close, and this indicates that the rate of change of the speed of sound as a function of temperature is almost identical for these derivatives. This, in turn, suggests that the capping groups contribute very little or none to the change in the speed of sound data with temperature. The speed of sound data have also been fitted with eq 7, and the estimated values of a, b, and r are given in Table 3. However, the intermolecular hydrogen-bonding appears to be the major cause for the magnitude of the speed of sound through a liquid. Excepting PPG, all of the end-capped derivatives exhibited speed of sound values which were nearly 40 m·s^{-1} faster than that PAG and about 50–60 m·s^{-1} faster than those of the end-capped derivatives. Thus, reducing the hydrogen-bonding effect of a molecule showed a major impact on its sonic properties.

Table 3. Estimated Coefficients of the Equation for the Speed of Sound, u, Calculated Adiabatic Bulk Modulus, B, and Specific Acoustic Impedance, z, of Various End-Capped PAG/PPG Derivatives

	u/(m·s^{-1})				
compound[a]	a	$-b$	r	10^9B/(kg·m^{-1}·s^{-1})	10^6z/(kg·m^{-2}·s^{-1})
I	1379	3.20	0.999	1.592	1.226
II	1381	3.17	0.999	1.623	1.246
III	1388	3.19	0.999	1.668	1.275
IV	1376	3.25	0.999	1.619	1.251
V	1378	3.27	0.999	1.615	1.246
VI	1387	3.18	0.999	1.734	1.326
PAG[b]	1395	3.34		1.673	1.276
PPG	1435	3.24	0.999	1.837	1.357
pure water[c]	1416	−2.85		2.205	1.483
sea water[d,e]				2.392	1.565
castor oil at 20 °C[f]				2.25	1.46

[a] Numbers I–VI refer to the same compounds as given in Table 1. [b] Reference 1. [c] Reference 11. [d] Reference 12. [e] Reference 13. [f] Reference 14.

The adiabatic bulk modulus, B, of a liquid is a useful property and is a measure of the difficulty of compressing a liquid; it is calculated as $B = \rho_0 u^2$. The units of B are kg·m^{-1}·s^{-1}. Another useful quantity is the specific impedance factor, z, which is the ratio of pressure to particle velocity in a material. It is a characteristic property of the medium and is useful in calculations involving the transmission of acoustic waves from one medium to another. It is calculated as $z = \rho_0 u$, and it has the units of kg·m^{-2}·s^{-1}. The values of these quantities have been calculated for the PPG/PAG derivatives and included in Table 3. Molecules which have the ability to intermolecularly hydrogen-bond, such as water, castor oil, and PPG, have high bulk modulus values. A high B value is desirable because it eliminates the necessity for a pressure-relief transducer design. Specific acoustic impedance values for PPG and its derivatives indicate that molecules with the ability to intermolecularly hydrogen-bond have the highest impedance values.

Water solubility data given in Table 1 indicate that dimethyl- and diethyl-end-capped PPGs have the highest water solubility among the derivatives investigated. However, among the alkane-end-capped derivatives, the methyl and ethyl groups are the smallest and, therefore, contribute the least amount of steric hindrance to the space around the terminal oxygen ether linkages, resulting in the ability of the water molecule to move in close proximity to the oxygen and hydrogen-bond with it. In general, the Karl-Fischer titration method gave larger percentage water values for the same compounds, but a longer water saturation time may have been a factor in the observed increase in water solubility.

Conclusion

On the basis of the results of this study for polypropylene glycol ether derivatives, the polypropylene ether backbone influenced the rate of change of the viscosity, density, and speed of sound as a function of temperature. Elimination of hydrogen-bonding by end-capping PAG/PPG with alkoxy groups decreased the viscosity dramatically, while capping with chlorine dropped the viscosity significantly, but not as much as for the alkoxy groups. The densities of the various PAG/PPG derivatives tend to increase, probably due to an increase in the degree of intermolecular association, as the size of the end-capping group decreases. A desirable increase in the speed of sound and adiabatic bulk modulus seemed to correlate with the ability of the molecules to hydrogen-bond.

Water solubility, a major concern for transducer fluids, was decreased by end-capping the PAG/PPG moiety. The large bulky capping groups exhibited the lowest solubility due in part to the steric hindrance they create for the water molecule to hydrogen-bond to the terminal ether oxygens. End-capping with an alkylfluoro group or with chlorine atoms decreased water solubility even further.

The present study lends stronger support to molecules containing a polypropylene ether backbone as a class of potential transducer fill fluids. Of the derivatives for which the complete series of physical tests were performed, the dichloro-end-capped PPG warrants further investigation as a promising transducer fill fluid. One aspect which needs further study is the stability and reactivity of this compound in the presence of a nucleophile. Ideally, a transducer fill fluid should have a specific acoustic impedance that is equal to that of sea water through which sound travels in order to diminish the proportion of the acoustic energy that is reflected.

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