Thermochimica Acta, 63 (1983) 51–58
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

HEATS OF IMMERSION OF AMORPHOUS As_2S_3, As_2S_5 AND As_2Se_3 IN ORGANIC LIQUIDS

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(Received 15 September 1982)

ABSTRACT

The heats of immersion of hydrophobic, amorphous arsenic chalcogenides have been measured in several organic liquids. For hexane, butanol, butylchloride and nitropropane, the heats of immersion with As_2S_3, As_2S_5 and As_2Se_3 showed linear dependences on the dipole moment of the wetting liquid molecule. From the results the average values of the electrostatic field strength were calculated to be 0.29×10^5, 0.31×10^5, and 0.57×10^5 e.s.u. cm^{-2}. The heats of immersional wetting of As_2S_3 and As_2Se_3 in *n*-alkanols linearly increased with an increase of *n*, the number of carbon atoms in $C_nH_{2n+1}OH$. The contributions due to polarization of the liquid molecule by the electrostatic field of the solid surface, due to the dispersion force and due to the interaction between the dipole moment of the liquid with the electrostatic field of the solid were calculated by applying the additivity of intermolecular forces. The result showed that the dispersion force was the dominant contribution to the interaction in As chalcogenides-*n*-alkanol systems.

INTRODUCTION

Chalcogenide glasses have been given a great deal of attention because of their peculiar electric and optical properties. The systems As–S and As–Se are the fundamental compositions of chalcogenide glasses. There have been a number of studies of these glasses. Most workers, however, have concentrated on physical properties, but very little has been done to investigate the surface chemistry.

The studies of surface properties are of importance in connection with the weathering and adhesive properties of these materials when applied in optical or electrical devices. In the present work, measurements have been made of the heats of immersion of amorphous As_2S_3, As_2S_5 and As_2Se_3 in several organic liquids. From the results the electrostatic field strength of the surface was estimated, and the contributions of the interaction of the dipole of the liquid molecule with the electrostatic field of the solid, dispersion force and polarization force to the total interaction energy were discussed.

0040-6031/83/$03.00

EXPERIMENTAL

Glasses were prepared from elemental arsenic, sulfur and selenium. The reagent mixture was placed in a silica glass ampoule and heated at 200° and 500°C for 1 h, then at 600°C for 10 h in a rocking-furnace, and then quenched at room temperature.

To perform an accurate calorimetry of immersion experiment, it is desirable to use a sample of high surface area. It is, however, difficult to prepare fine powder of large specific surface area from glasses by pulverizing. In the present work, fine powders of amorphous As_2S_3 and As_2S_5 were also prepared by precipitation from the acidic solutions containing $As(III)O_3^{3-}$ and $As(V)O_4^{3-}$ ions by passing H_2S.

Ten grams of As_2O_3 were dissolved in 100 ml of 1 N NaOH solution, and the pH adjusted to 1–2 by addition of HCl solution. Then H_2S was passed through the solution to precipitate amorphous As_2S_3. Amorphous As_2S_5 was precipitated as described. Ten grams of As_2O_3 were dissolved in 20 ml of conc. HNO_3 ($d = 1.38$) and warmed at 80–90°C on a water bath to oxidize As(III) to As(V). Warming was allowed to continue for about 8 h until no evolution of NO gas was observed. Then the solution was evaporated to dryness at 250°C in an oil bath. The residue was dissolved in a little amount of water, filtered and dehydrated by gentle heating to obtain As_2O_5. One gram of the As_2O_5 was dissolved in 50 ml of water and conc. HCl ($d = 1.18$) was added little by little to the solution under cooling in an ice bath. Then H_2S was passed through the solution under cooling to precipitate As_2S_5.

In the preparation of As_2S_5 as described, the product often decomposes to As_2S_3 and S when the cooling is mild and the acid concentration is low. In the present experiment, As_2S_5 was identified as described.

Carbon disulfide dissolves the sulfur with ring-structure but not that with chain-structure, S_n [1]. No appreciable amount of sulfur was extracted from the product obtained, while about 20 wt.% of sulfur was extracted from the sample which had been prepared under insufficient cooling and low concentration of HCl.

The powder X-ray diffraction pattern showed the sample prepared by our procedure to be fully amorphous, but for an inappropriately prepared sample the peaks which could be assigned to α–S were observed. Finally, the atomic ratio of S/As was confirmed to be 2.5 by chemical analysis.

All the liquid chemicals used for immersion experiments were obtained commercially and no further purification was made except for removal of water, which was achieved by the use of molecular sieves prior to measurements.

A twin-microcalorimeter, Tokyo Riko TIS-2S, was used for measurements of heat of immersion. The calorimeter and the techniques have been described elsewhere [2] in detail. All the immersion experiments were performed at 30°C. The specific surface areas of the samples, as determined by nitrogen adsorption, are shown in Table 1.

TABLE 1

Specific surface areas of samples

Sample	Specific surface area ($m^2\ g^{-1}$)
As_2S_3(ppt) [a]	17.6
As_2S_3(gl) [b]	4.6
As_2S_5(ppt)	10.8
As_2Se_3(gl)	1.7

[a] Prepared by precipitation.

[b] Glass

RESULTS AND DISCUSSION

Electrostatic field of surfaces

Zettlemoyer and co-workers [3–5] proposed that the electrostatic field of solid surface could be estimated from the heat of immersion. With the assumption that vertical, lateral and other internal interactions of the molecules in the adsorbed state are the same as in the liquid state, the difference between the energy of adsorbed molecule, E_A, and of liquid molecule, E_L, is given as

$$E_A - E_L = E_\mu + E_\alpha + E_d \qquad (1)$$

where E_μ is the energy of interaction between the electrostatic field of the solid surface and the dipole moment of the wetting liquid molecule, E_α is the energy of interaction between the electrostatic field and the induced dipole moment of the liquid, and E_d is the energy of interaction by London dispersion force. Multiplication of the left hand side of eqn. (1) by Γ gives the net heat of adsorption ΔH_a on a unit area basis, which is related to heat of immersion ΔH_i (on a unit area basis) by

$$\Delta H_a = \Delta H_i + \Delta H_L = \Gamma(E_A - E_L) \qquad (2)$$

where ΔH_L is the surface enthalpy of the wetting liquid, and Γ is the number of molecules adsorbed on a unit surface area.

From eqns. (1) and (2)

$$\Delta H_i + \Delta H_L = \Gamma(E_\mu + E_a + E_d) \qquad (3)$$

When the immersion experiments for a given solid are made in a series of liquids which are similar in molecular volumes and polarizabilities, i.e. $(E_\alpha + E_d)$ is comparable for every liquid, the left hand side of eqn. (3)

TABLE 2

Heats of immersion in hexane, butanol, butylchloride and nitropropane

Sample	ΔH_i (erg cm^{-2})			
	n-C_6H_{14}	n-C_4H_9OH	n-C_4H_9Cl	n-$C_3H_7NO_2$
As_2S_3(ppt)	−130	−154	−166	−186
As_2S_3(gl)	−128	−156	−163	−195
As_2S_5	−146	−245	−180	−210
As_2Se_3	−272	−311	−342	−381

depends only on E_μ. Since E_μ is given by

$$E_\mu = -\mu F \tag{4}$$

where μ is the dipole moment of the liquid and F is the electrostatic field strength of the solid surface, values of $(\Delta H_i + \Delta H_L)$ must give linear plots against μ.

Zettlemoyer and co-workers [3] reported that for a series of n-butyl derivatives the heats of immersion with TiO_2(rutile), CaF_2 and SiO_2(Aerosil) were shown to be approximate linear functions of μ. In the present work, the immersion experiments have been done in n-hexane, n-butanol, n-butylchloride and n-nitropropane. The heats of immersion are shown in Table 2. The surface enthalpy at 30°C was obtained by

$$\Delta H_L = \gamma_L - T\left(\frac{\delta \gamma_L}{\delta T}\right)_p \tag{5}$$

where γ_L is the surface tension and T is absolute temperature. The numerical

TABLE 3

Numerical values used for calculations.

Liquid	μ [a] (debye)	ΔH_L (erg cm^{-2})	$\alpha \times 10^{24}$ [a] (ml)
CH_3OH	1.66	48	3.26
C_2H_5OH	1.68	47	5.13
n-C_3H_7OH	1.66	46	6.96
n-C_4H_9OH	1.68	47	8.63
n-$C_5H_{11}OH$	1.80	51	10.63
n-$C_3H_7NO_2$	3.57	57	8.59
n-C_4H_9Cl	2.11	54	8.65
n-C_6H_{14}	0	48	11.87

[a] Values obtained from ref. [6].

values available for the calculations are shown in Table 3. The value of $(\Delta H_i + \Delta H_L)$ is plotted against μ of the wetting liquid in Fig. 1. As can be seen from Table 2, ΔH_i values of As_2S_3(gl) agreed closely with those of As_2S_3(ppt) within the experimental error. The mean values of the heats of immersion of glassy and precipitated samples were taken for the Fig. 1 plots.

The plots for every sample lie on a separate line. From eqns. (3) and (4)

$$\frac{(\Delta H_i + \Delta H_L)}{\Gamma} - \mu F + (E_\alpha + E_d) \tag{6}$$

The electrostatic field strength, F, therefore, can be obtained from the slope of the straight line in Fig. 1. In the present case, Γ was taken as 5×10^{14} molecule cm^{-2} by taking the cross-sectional area of a polymethylene chain as 20.5 $Å^2$. Thus, F values were calculated to be 0.29×10^5, 0.31×10^5 and 0.57×10^5 e.s.u. cm^{-2} for As_2S_3, As_2S_5 and As_2Se_3, respectively. These values, which are considerably lower than those of TiO_2 (rutile, 2.7×10^5) [3], CaF_2 (2.0×10^5) [4] and SiO_2(Aerosil, 1.1×10^5) [4], show that the electrostatic field extending from the As chalcogenide surface is very weak.

Contributions from polarization and dispersion forces

In water the heat of immersion of As_2S_3 was very low, and for As_2S_5 and As_2Se_3, ΔH_i values could not be obtained because the sample powder came to the liquid surface on immersion without wetting. These results suggest that the materials have hydrophobic surfaces. The immersion experiments were made for a series of *n*-alkanols. The results are shown in Table 4. In Fig. 2 the heats of immersion are plotted against the number of carbon atoms in the alkanol, $C_nH_{2n+1}OH$. The heat of wetting $(-\Delta H_i)$ increases with an increase of n.

As stated before, E_μ can be obtained from eqn. (4) by using F values

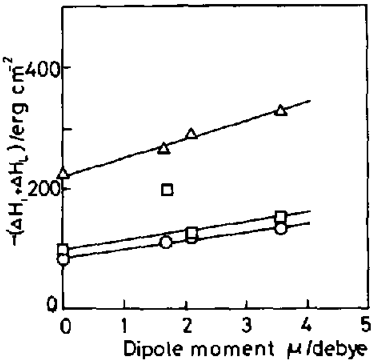

Fig. 1. Plot of $-(\Delta H_i + \Delta H_L)$ as functions of the dipole moment of polar molecules. ○, As_2S_3; □, As_2S_5; △, As_2Se_3.

TABLE 4

Heats of immersion in *n*-alkanols

Sample	ΔH_i(erg cm^{-2})				
	CH_3OH	C_2H_5OH	*n*-C_3H_7OH	*n*-C_4H_9OH	*n*-$C_5H_{11}OH$
As_2S_3	−95	−106	−137	−154	−172
As_2S_5	−151	−221	−240	−245	−243
As_2Se_3	−193	−218	−263	−311	−336

obtained in the present work. The contribution of the polarization force, E_α, can be calculated by

$$E_\alpha = -\tfrac{1}{2}\alpha F^2 \tag{7}$$

where α is the polarizability of the liquid molecule. When the values of $\Gamma(E_\mu + E_\alpha)$ are subtracted from $(\Delta H_i + \Delta H_L)$, ΓE_d values are obtained. Tables 5–7 show the various calculated interaction energies, which are reduced to a unit area basis, for the As chalcogenides–alkanols and some other liquids systems. The numerical values of α are available in the literature [6].

As seen from the tables, E_μ and E_α are only very slightly dependent on n. In Fig. 2, $-\Delta H_i$ values of As_2S_3 and As_2Se_3 show an approximately linear increase with n. The gain in ΔH_i, obtained by an increment of CH_2 in the alkanol molecule, is about −20 erg cm^{-2} for As_2S_3 and −38 erg cm^{-2} for As_2Se_3. The calculated values of $-\Gamma E_d$ of As_2S_3 and As_2Se_3 are plotted against n in Fig. 3. Similar dependences are found in Fig. 2. The gain in ΓE_d by the increment of CH_2 in the alkanol is about −19 erg cm^{-2} for As_2S_3 and −35 erg cm^{-2} for As_2Se_3.

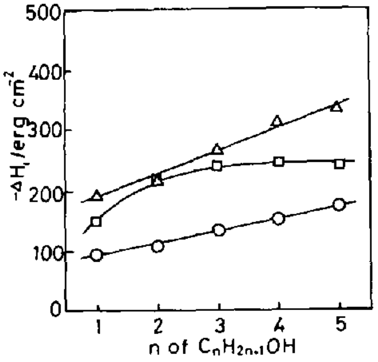

Fig. 2. Plot of $-\Delta H_i$ against carbon number of *n*-alkanols. ○, As_2S_3; □, As_2S_5; △, As_2Se_3.

TABLE 5

Contributions by E_{μ}, E_{α}, and E_{d} for As_2S_3-liquid systems

Liquid	Interaction energy (erg cm^{-2})		
	ΓE_{μ}	ΓE_{α}	ΓE_{d}
CH_3OH	−24	−1	−22
C_2H_5OH	−24	−1	−34
n-C_3H_7OH	−24	−2	−65
n-C_4H_9OH	−24	−2	−81
n-$C_5H_{11}OH$	−26	−2	−93
n-$C_3H_7NO_2$	−52	−2	−75
n-C_4H_9Cl	−31	−2	−79
n-C_6H_{14}	0	−3	−79

TABLE 6

Contributions by E_{μ}, E_{α}, and E_{d} for As_2S_5-liquid systems

Liquid	Interaction energy (erg cm^{-2})		
	ΓE_{μ}	ΓE_{α}	ΓE_{d}
CH_3OH	−26	−1	−76
C_2H_5OH	−26	−1	−147
n-C_3H_7OH	−26	−2	−166
n-C_4H_9OH	−26	−2	−170
n-$C_5H_{11}OH$	−28	−3	−161
n-$C_3H_7NO_2$	−55	−2	−96
n-C_4H_9Cl	−33	−2	−91
n-C_6H_{14}	0	−3	−95

TABLE 7

Contributions by E_{μ}, E_{α} and E_{d} for As_2Se_3-liquid systems

Liquid	Interaction energy/(erg cm^{-2})		
	ΓE_{μ}	ΓE_{α}	ΓE_{d}
CH_3OH	−47	−3	−95
C_2H_5OH	−48	−4	−119
n-C_3H_7OH	−47	−6	−164
n-C_4H_9OH	−48	−7	−209
n-$C_5H_{11}OH$	−51	−9	−225
n-$C_3H_7NO_2$	−102	−7	−215
n-C_4H_9Cl	−60	−7	−221
n-C_6H_{14}	0	−10	−214

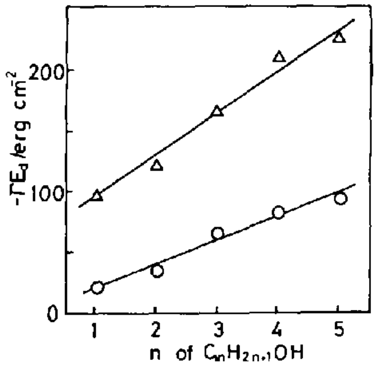

Fig. 3. Dispersion force contribution as functions of carbon number in *n*-alkanols. ○, As_2S_3; △, As_2Se_3.

These results lead to the conclusion that the dominant contribution to the interaction in As chalcogenides–*n*-alkanol systems is the dispersion force.

CONCLUSION

Amorphous arsenic sulfide and selenide were immersed in several organic liquids, which were similar in molecular shape and volume but different in dipole moment, to estimate the electrostatic field strength from the observed heats of immersion. The average electrostatic field strengths calculated to be 0.29×10^5, 0.31×10^5 and 0.57×10^5 (e.s.u. cm^{-2}) for As_2S_3, As_2S_5 and As_2Se_3, respectively, suggest that the surfaces of these materials are very weakly polar.

The heats of immersion of As_2S_3 and As_2Se_3 in a series of *n*-alkanols, $C_nH_{2n+1}OH$, were found to be linear functions of *n*. The calculation of the contributions due to the dispersion force, the polarization and the interaction between the electrostatic field of the solid surface and the dipole moment of the liquid have been done. The result shows that the dispersion force is the dominant contribution to the interaction between the As chalcogenide surfaces and the alcohols.

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