Some Observations on the Sorption of Moisture by Elastomeric Solid Propellant Binders

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Synopsis

The isotherms for the sorption of water by six rubbery binders of the sort used in solid propellants have been measured at room temperature. The solubility at saturation ranged from 0.003 to 0.030 g. of water/g. of binder. The Flory-Huggins equation was used to calculate an upper limit for the χ_1 interaction parameters; these ranged from 2.6 to 4.7. The isotherms were best fitted by a modified Henry's law equation:

$$p/p_0 = (1/k) [N_1/(N_1 + N_2)] = (1/k) S/[S + (\alpha - 1)S_{max}]$$

The possible significance of the parameters k, α, β, and S_{max} is discussed.

INTRODUCTION

The binders used in most solid propellants are lightly crosslinked network polymers, vary considerably in chemical composition, but because of their end use, nearly all are rubbery and have roughly the same mechanical properties. All are affected to some degree by absorbed moisture; cases are known wherein the sorption of as little as 1% moisture by a solid propellant has reduced the tensile strength by 30%.[1] Most of the reported data on the effect of moisture on mechanical properties has been in terms of the relative humidity of the environment rather than the actual amount of water taken up.

Because propellant–water systems not only take up more water than the corresponding amount of pure binder but also show nonreversible effects, initial experiments, which are the only ones that are reported here, were done on the system binder–water. With this in mind, six binders, made from a variety of commercial materials, have been studied. The sorption isotherms at room temperatures have been determined and possible relationships discussed.

APPARATUS AND PROCEDURE

The apparatus was based on the concept of McBain and Baker.[2] The polymer samples were about 0.5 mm. thick, 2.0–2.5 cm. wide and 5.0–7.0 cm. long and weighed 0.7–1.0 g. The sample was suspended from a coil spring, and changes in weight were measured by observing the change in

the length of the spring.   The helix was 12–14 mm. in diameter, about 100 turns in length, and was made from 32 gauge Nichrome wire.   A quartz helix would have been better, since the Nichrome coil showed observable creep under load on standing overnight (0.2 mm. in 24 hr. under 1 g. load; less than experimental error under 0.7 g. load).   The changes in spring length were observed by a Gaertner cathetometer reading to 0.05 mm. A correction of approximately 0.05 mm./°C. was made for the variation of the spring length with temperature.

The system was evacuated by means of a mechanical pump to about 0.1 mm. total pressure.   The permanent gases present were ordinarily less than this, since the system could be flushed with water vapor during the pumping.   Water vapor was supplied by a salt solution, the temperature of which, and hence the water vapor pressure, was controlled by adjusting the temperature of the surrounding water bath.   (A solution of sodium chloride was used instead of pure water, because the lower vapor pressure of the salt solution eliminated the problem of condensation on the coil if the apparatus were allowed to stand at ambient temperature overnight.) Since the sample chamber was not thermostatically controlled, the specimen was assumed to be at room temperature (the variation was only about 3°C. during the course of the day and usually less than 1°C. during the experiment).   The temperature of the salt solution was assumed to be the temperature of the bath.   After equilibrium was attained, either the temperature of the bath was changed and a new equilibrium established (indicated in Tables I–VII as Eq), or the stopcock to the salt solution was closed and the one to the drying agent (Drierite with cobalt indicator) opened, and a new equilibrium dry weight obtained (Des in tables).   Thus equilibrium was approached from both directions and both rapidly and slowly in the various experiments.   The agreement between absorption and desorption experiments indicates that equating weight changes with sorption or desorption of water is correct within experimental error (less than 1 mg.).   In both the absorption and desorption runs, weight changes as a function of time were recorded so that the approach to equilibrium could be estimated.

RESULTS AND DISCUSSION

Plots of the weight (milligrams) of water absorbed per gram of binder (S) versus the relative vapor pressure of water (p/p_0) were made for each sample.   Figures 1 and 2 show several of these; the data are given in Tables I–VII.   The curves are all of the same general shape; they are concave upward and extrapolate, within experimental error, to the origin without need for a point of inflection (type III isotherms).   As is usual with experimental data, the curves can be fitted quite well by any of several mathematical expressions.   Two of the possible equations for the isotherms are discussed below.
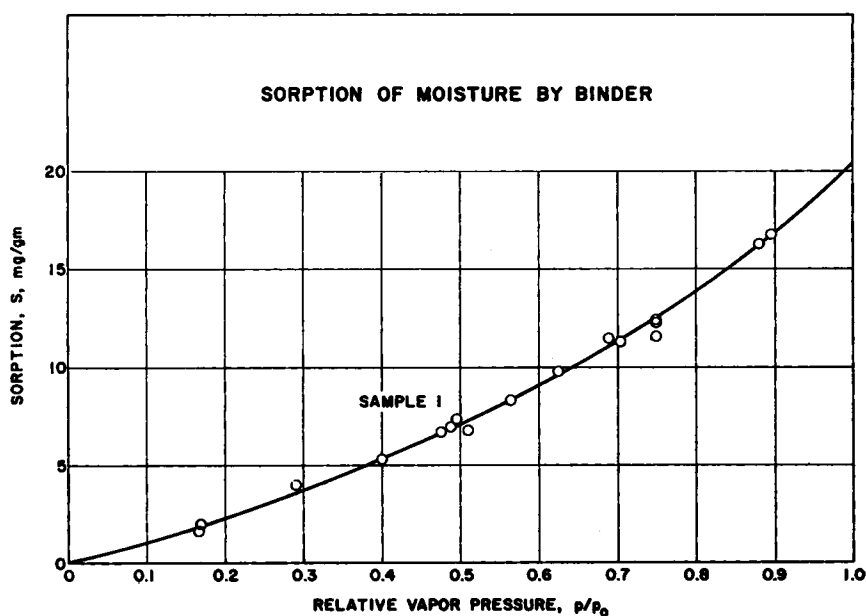
Fig. 1. Plot of milligrams of water absorbed per gram of binder (polyurethane type) vs. the relative vapor pressure of water. Equation (4) in the form: $S = (\beta p/p_0)/(\alpha - p/p_0)$ with $N_1 = S/18$, $N_2 = \beta/18$, $\alpha = 2.2$, and $\beta = 0.0229$ was used to calculate the line.

TABLE I

Sorption of Moisture by Binder for Sample 1[a,b]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	x_1
1	Des	22.0	0.750	11.6	3.25
2	Abs	22.8	0.750	12.3	3.20
3	Des	23.6	0.750	12.4	3.19
4	Abs	22.8	0.167	1.64	3.64
5	Des	22.7	0.167	1.64	3.64
6	Abs	23.1	0.292	3.69	3.40
6a	Eq	23.2	0.170	2.05	3.43
6b	Eq	23.4	0.497	7.37	3.27
6c	Eq	23.0	0.400	5.34	3.36
6d	Eq	24.0	0.565	8.36	3.28
6e	Eq	24.1	0.625	9.84	3.24
6f	Eq	22.4	0.704	11.3	3.21
7	Des	22.8	0.689	11.5	3.18
8	Abs	23.4	0.898	16.7	3.11
9	Des	23.7	0.882	16.2	3.11
10	Abs	22.9	0.475	6.72	3.31
11	Des	22.5	0.487	6.96	3.30
12	Abs	22.5	0.510	6.80	3.37

[a] Weight: 0.875 g.; thickness = 0.0533 cm.

[b] In this and in the following tables the data are given to three significant figures to avoid rounding off errors; p/p_0 is not known to better than 1% and S not better than ±0.4 mg/g.
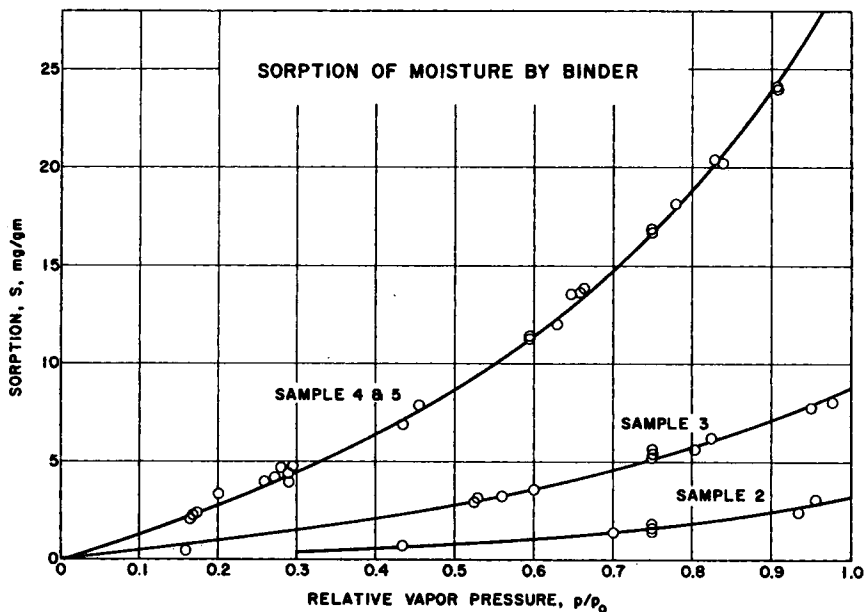
Fig. 2. Plot of milligrams of water absorbed per gram of binder vs. relative vapor pressure of water for three binder types: carboxy-terminated butadiene (sample 2), butadiene–acrylonitrile–acrylic acid terpolymer (sample 3), and polyurethane (samples 4 and 5). Like Figure 1, the lines were calculated from eq. (4) by using the values of α and β given in Table VIII ($\alpha = 1/k$).

TABLE II

Sorption of Moisture by Binder for Sample 2[a]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	χ_1
13	Abs	22.2	0.75	1.51	5.23
14	Des	23.2	0.75	1.81	5.05
15	Abs	22.8	0.935[b]	2.42	4.98
15a	Eq	22.1	0.956	3.03	4.79
16	Abs	22.6	0.700	1.36	5.26
17	Abs	22.6	0.75	1.51	5.23
18	Des	24.4	0.75	1.66	5.13
18a	Eq	23.6	0.435	0.68	5.47

[a] Weight: 0.9485 g.; thickness = 0.0425 cm.
[b] ±0.020.

Flory-Huggins Equation

Although the equation developed by Flory[3,4] and Huggins[5] for the free energy of dilution of polymer solutions,

$$\Delta \bar{F}_1 = \mu_1 - \mu_1{}^0 = RT[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2{}^2] \quad (1a)$$

$$\ln p/p_0 = \ln v_1 + v_2 + \chi_1 v_2{}^2 \quad (1b)$$

TABLE III
Sorption of Moisture by Binder for Sample 3[a]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	χ_1
19	Abs	22.8	0.75	5.25	3.95
19a	Eq	25.3	0.158	0.45	4.86
20	Abs	22.8	0.525	2.98	4.16
20a	Eq	23.5	0.530	3.21	4.10
21	Abs	24.1	0.560	3.29	4.13
21a	Eq	23.1	0.598	3.59	4.14
22	Abs	23.8	0.825	6.20	3.89
22a	Eq	23.8	0.805	5.58	3.96
23	Abs	23.1	0.950	7.73	3.81
23a	Eq	22.0	0.978	8.03	3.80
24	Des	21.7	0.75	5.36	3.94
24a	Eq	21.8	0.75	5.66	3.89

[a] Weight: 0.9377 g.; thickness = 0.0635 cm.

TABLE IV
Sorption of Moisture by Binder for Sample 4[a]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	χ_1
25	Abs	24.0	0.75	16.7	2.92
26	Des	24.4	0.75	16.9	2.91
27	Abs	22.8	0.167	2.06	3.37
28	Des	23.3	0.167	2.06	3.37
29	Abs	23.9	0.201	3.38	3.11
29a	Eq	24.5	0.272	4.22	3.20
29b	Eq	24.5	0.290	4.37	3.23
30	Abs	24.4	0.595	11.5	3.07
31	Des	24.2	0.595	11.3	3.06
32	Abs	23.6	0.909	23.9	2.80
33	Des	23.2	0.909	24.1	2.79
34	Abs	23.6	0.665	13.9	2.97
35	Des	23.6	0.657	13.6	2.97
36	Abs	22.0	0.168	2.23	3.34
37	Des	22.6	0.168	2.28	3.34
38	Des	23.2	0.290	3.96	3.32
38a	Eq	22.9	0.258	3.96	3.21
38b	Eq	23.2	0.280	4.71	3.12
38c	Eq	23.2	0.295	4.79	3.16

[a] Weight: 0.869 g.; thickness = 0.0330 cm.

was originally derived for dilute solutions of linear polymers in essentially nonpolar solvents, its use has been extended to a number of additional cases; for example, Starkweather[6] found that the Flory-Huggins equation represents the type III isotherms for the nylon 66–water and the nylon

TABLE V
Sorption of Moisture by Binder for Sample 5[a]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	χ_1
39	Abs	23.1	0.630	12.0	3.04
39a	Eq	23.0	0.647	13.6	2.96
39b	Eq	23.4	0.781	18.2	2.88
39c	Eq	23.6	0.840	20.2	2.86
39d	Eq	23.7	0.830	20.4	2.84
40	Abs	21.9	0.174	2.41	3.30
41	Des	22.2	0.174	2.41	3.30
42	Abs	23.8	0.434	6.90	3.19
43	Des	23.7	0.455	7.93	3.11

[a] Weight: 0.895 g.; thickness = 0.0437 cm.

TABLE VI
Sorption of Moisture by Binder for Sample 7[a]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	χ_1
51	Abs	25.5	0.550	4.98	3.75
52	Des	25.7	0.544	4.72	3.79
53	Abs	23.0	0.768	7.35	3.76
54	Abs	23.5	0.870	9.77	3.57
55	Des	24.0	0.885	9.65	3.60

[a] Weight: 0.8054 g.; thickness = 0.0450 cm.

TABLE VII
Sorption of Moisture by Binder for Sample 8[a]

Run no.	Absorption or desorption	Avg. temp., °C.	p/p_0	S, mg./g.	χ_1
59	Abs	23.8	0.630	4.53	3.98
60	Abs	23.4	0.870	7.61	3.80
61	Des	23.8	0.860	7.44	3.81
62	Abs	23.3	0.162	0.91	4.19
63	Des	23.6	0.162	0.91	4.19
64	Abs	23.8	0.270	1.75	4.05
65	Abs	21.8	0.485	3.14	4.07
66	Des	22.0	0.500	3.26	4.06

[a] Weight: 0.8752 g.; thickness = 0.0567 cm.

610–water systems very well (over almost the entire range of his measurements).

Since our isotherms are also type III, it appeared that the Flory-Huggins equation might fit our data. The experimental data needed are the relative partial pressure, p/p_0, and the volume fractions of solvent and poly-
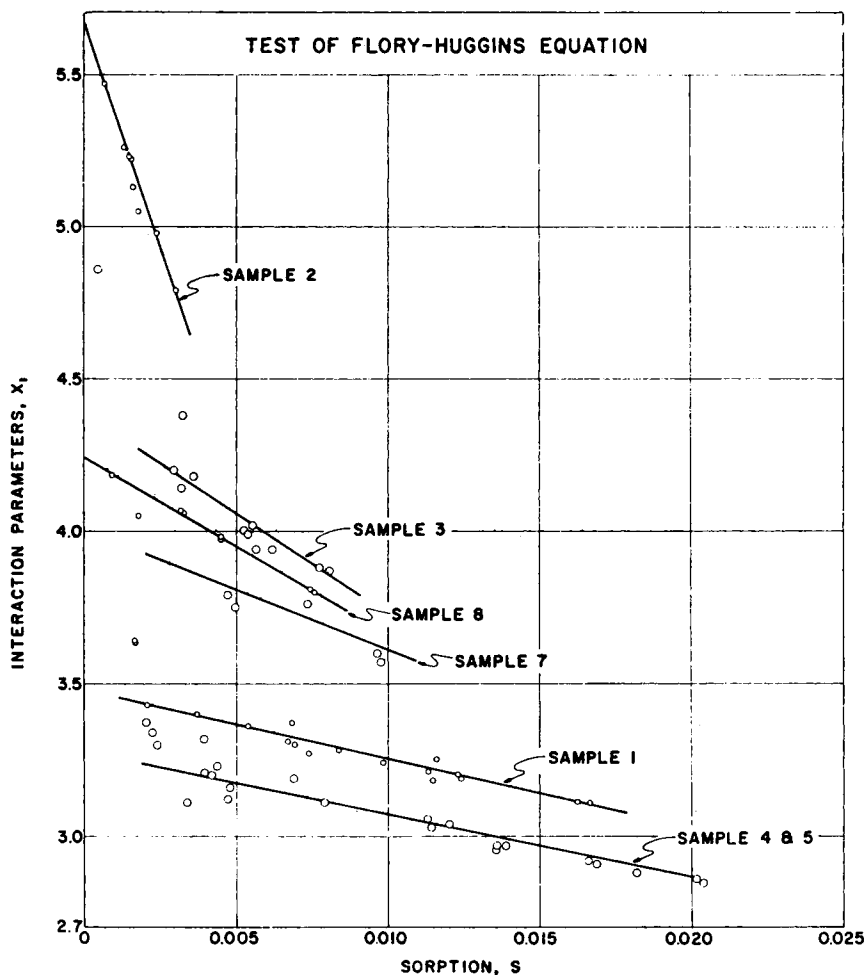
Fig. 3. Plot of interaction parameter χ_1 vs. sorption S (equivalent to χ_1 vs. v_2). Note the systematic deviation of the lines from horizontality; the logarithm of the slope of the lines is roughly proportional to χ_1.

mer. We have not measured the volume changes as water was sorbed, but for the small amounts taken up, the weight of water S sorbed per gram of polymer should be a good approximation for v_1, the volume fraction of water, since the densities of the polymers studied are approximately unity. By definition $(v_1 + v_2) = 1$, so we may take $v_2 = (1 - S)$, and hence eq. (1b) may be written

$$\ln p/p_0 = \ln S + (1 - S) + \chi_1 (1 - S)^2 \qquad (2)$$

Equation (2) was used to calculate the interaction parameter for each of our experimental points; the χ_1 values for the six polymer–water systems are plotted against S in Figure 3. Since S is approximately $1 - v_2$, this

plot is equivalent to the usual χ_1 versus v_2 representation. As expected, the χ_1 values are greatest for the polymer in which water is the least soluble, and smallest for the most soluble. Considering the polar character of water and its low solubility in these polymers, the χ_1 values seem reasonable. Systematic trends are immediately seen; χ_1 was most nearly constant in the most soluble system (samples 4 and 5) and least constant for the least soluble; the slope of each line appears to be related to the magnitude of χ_1 (log slope proportional to χ_1). Constancy of χ_1 is a measure of the fit of eq. (2). Thus, eq. (2) fits the more soluble systems (1, 4, and 5) reasonably well, but fits the least soluble system rather poorly. The χ_1 values for nylon 66, given by Starkweather[6] in his Table I, vary only from 1.45 to 1.48 as the water content varies from 7.2 to 1.4% but at 0.66 and 0.16% water χ_1 is 1.59 and 2.02; likewise, for nylon 610, the χ_1 value for the lowest water content, 0.4%, is 2.29, noticeably above 2.18 ±2 for the remaining points. When these are corrected for the crystalline content ($\sim$50%), it is seen that Starkweather's data depart from eq. (1b) in the region below 3–4% water just as ours do. It has long been known that the Flory-Huggins equation does not ordinarily fit low concentrations of polymer in large amounts of solvent[7,8] and from our data and the data for nylon it appears that it does not hold for low concentrations of water in polymer. Thus we conclude that for each of our systems, eq. (2) does not give the true value of χ_1, but that the lowest χ_1 value, i.e., the one corresponding to $p/p_0 = 1$ does represent an upper limit of the true value.

In Table VIII, we list for each sample, $S_{\max}$ (the estimate solubility at $p/p_0 = 1$), the corresponding value of χ_1, and the partial molal heat of mixing or the heat of dilution calculated from

$$\Delta \bar{H}_1 = RT\chi_1 v_2{}^2 \cong RT\chi_1 (1 - S_{\max})^2 \qquad (3)$$

TABLE VIII
Estimated Interaction Parameters at Maximum Solubility

Sample	Identification	$S_{\max}$, g./g.	χ_1	$\Delta\bar{H}_1$, cal./ mole^2
2	Carboxy-terminated butadiene	0.0034	4.73	2770
3	Butadiene–acrylonitrile– acrylic acid terpolymer	0.0086	3.82	2210
8	Polyurethane, C-1 type	0.0099	3.64	2100
7	Nitroplasticized polyure- thane	0.0120	3.50	2010
1	Polyurethane	0.0205	3.02	1710
4 and 5	Polyurethane	0.0288	2.64	1460

The $\Delta\bar{H}_1$ values obtained (1460–1770 cal/mole) seem reasonable but are undoubtedly somewhat high, since the χ_1 values used were actually upper limits.

Henry's Law

The second equation for the isotherm which we wish to discuss is Henry's law:

$$p/p_0 = \alpha [N_1/(N_1 + N_2)] \tag{4}$$

where N_1 = moles of component 1, N_2 = moles of component 2.

For a network polymer, the estimation of N_2, the number of moles of polymer (or polymer units), is bound to be somewhat arbitrary; in this case, we define a polymer unit as that amount of polymer which contains one sorption site (for water). This quantity is not known *a priori* but may be evaluated from the experimental data.

Dole[9] has discussed the general sorption isotherm,

$$N/N_s = a\, \phi'/\phi \tag{5}$$

where: N = number of moles of vapor sorbed per unit absorbent, N_s = number of moles of sorption sites per unit absorbent, a = relative partial pressure = p/p_0,

$$\phi' = d\phi/da$$

and

$$\phi = 1 + a + c_1 a + c_1 c_2 a^2 + c_1 c_2 c_3 a^3 + \ldots \tag{6}$$

The constants, $c_1, c_2, c_3, \ldots$, are the ratio of the internal partial functions of the sorbed molecules in the first, second, third, $\ldots$, etc., layers to the partition function of pure liquid.

Dole[9] finds that by selection of the proper values for the constants, c_j, eq. (5) reduces to the Langmuir isotherm (c_1 constant, all other $c_j = 0$), to the B.E.T. isotherm (all $c_j = 1$ except c_1), to Raoult's Law (all $c_j = 1$), and for all $c_j = k$ ($k < 1$) to the form:

$$a/N = (1/k)\,(1/N) - (a/N_s)$$

which may also be written

$$a = p/p_0 = (1/k)\,[N/(N + N_s)] \tag{7}$$

On comparing eq. (7) with eq. (4) we see that $1/k$ (the reciprocal of the ratio of the partition functions) corresponds to the Henry's law constant, α, and that N_s, the number of moles of sorption sites replaces N_2.

The unknown quantities, k and N_s (or N_2) are easily evaluated from the experimental data by rearranging eq. (7) to the form:

$$1/(p/p_0) = k + kN_s\,(1/N_1) \tag{8}$$

and plotting $1/(p/p_0)$ against $1/N_1$ (the slope is kN_s; the intercept k). Since the mole fraction, $N_1/(N_1 + N_s)$, is a dimensionless quantity, by setting $N_1 = S/18$ and $N_s = \beta/18$ the experimental data can be evaluated without converting each measurement to moles of water per gram of poly-
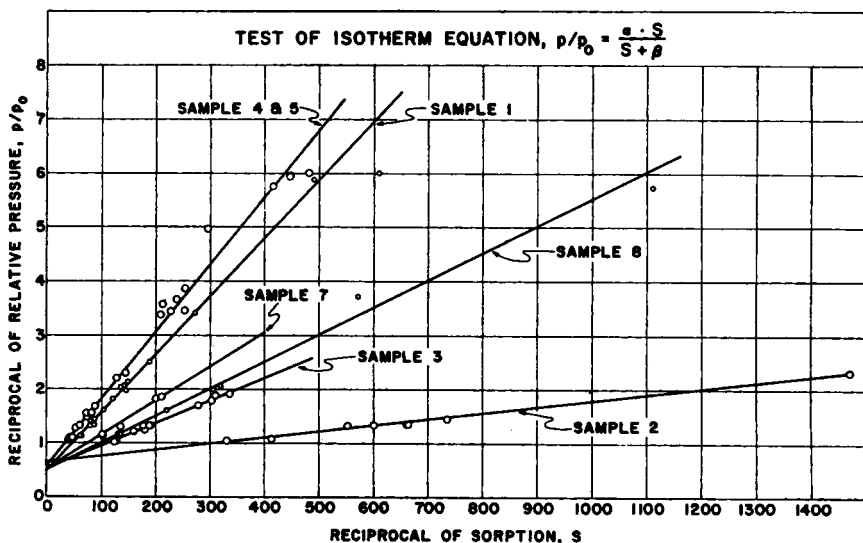
Fig. 4. This plot of the reciprocal of the relative vapor pressure of water vs. the sorption was used to calculate the constants in the isotherm eq. (7); the values are listed in Table VIII.

mer. The data are so plotted in Figure 4. The points at low values of p/p_0 scatter somewhat, as is to be expected, but the overall fit is good. Slopes, intercepts, $1/k$, β and N_s are listed in Table IX; $k\beta/(1 - k)$ is also listed, since for $p/p_0 = 1$, $S_{max} = k\beta/(1 - k)$.

The data for sample 1 are also plotted as a function of the mole fraction, x_1, in Figure 5. The data fall on a straight line of slope $1/k$ from the origin to the value of x_1 corresponding to S_{max} (in this case 0.472) at which point a new phase, water saturated with respect to polymer appears. The diagonal is the Raoult's law line for ideal solution. This figure also reminds us that the binder-water systems discussed here are not only non-ideal but have a large immiscibility gap.

TABLE IX
Fit of Experimental Data to Equation (8)

Sample	Slope	Intercept	$1/k$	β	$1/N_s$	S_{max}, mg./g. Calc.[a]	S_{max}, mg./g. Extrap.[b]
1	0.0108	0.47	2.12	0.0229	785	0.0205	0.0205
2	0.00109	0.65	1.54	0.00168	10700	0.0031	0.0034
3	0.00424	0.51	1.96	0.00830	2160	0.0086	0.0086
4	0.0120	0.61	1.64	0.0196	915	0.0307	0.0288
7	0.00634	0.50	2.00	0.0127	1420	0.0127	0.0125
8	0.00498	0.52	1.92	0.00956	1880	0.0104	0.0100

[a] $S_{max} = k\beta/(1 - k)$.
[b] Graphical interpolation (Figs. 1 and 2).
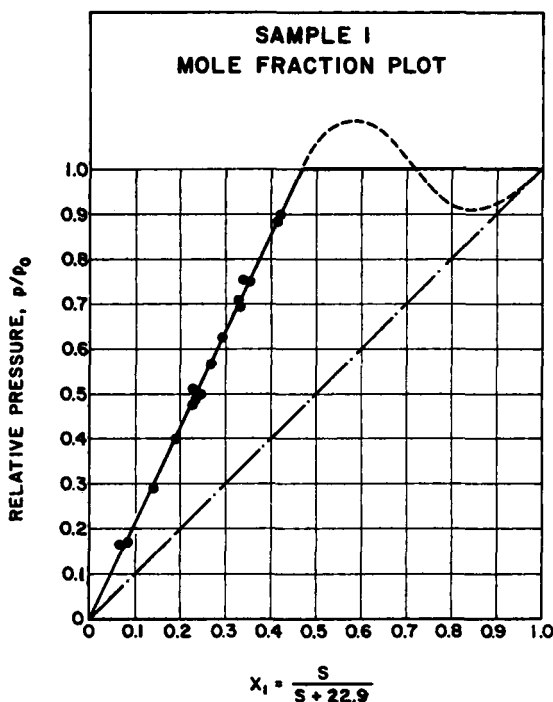
$$x_1 = \frac{S}{S + 22.9}$$

Fig. 5. This plot, relative vapor pressure vs. the mole fraction of water, is the phase diagram for the system water–polyurethane binder (sample 1) at 23°C. The slope of the experimental line is the Henry's law constant and is numerically equal to α (i.e., 2.12). Beyond a mole fraction of 0.43, an immiscibility gap appears, the new phase presumably being water saturated with binder. The diagonal line indicates Raoult's law. The units for S are mg./g.

The identification of N_2 in eq. (4) with N_s, the number of moles of sorption sites per unit weight of polymer, leads to interesting possibilities. The reciprocal of N_s is a molecular weight and, for our samples, ranges from 800 to 10,000, the same order of magnitude as M_c, the molecular weight between crosslinks, suggesting that only a few sites are available for each chain. A more exact statement cannot be made at this time, since the binders we have studied so far are all made from commercial materials and the compositions are not accurately known nor have they been systematically varied. However, the possibility of estimating the number of sites on the basis of chemical structure and hence of predicting the relative sorption of water in binders appears promising. Likewise, if the ratio of $1/N_s$ to M_c is established, additional thermodynamic quantities may be estimated.

Incidentally, we expect that the moisture isotherms of solid propellants made from rubbery binders may be fitted by eq. (8) up to values of p/p_0 corresponding to the hygroscopic point of ammonium perchlorate (approximately 0.90).

Further speculation is not warranted until systematic studies have been made.

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Résumé

On a déterminé les isothermes à température de chambre de l'absorption d'eau par six liants caoutchouteux de l'espèce utilisée dans les propulseurs solides. La solubilité à saturation est de 0.003 à 0.030 gr d'eau par gramme de liant. L'équation de Flory-Huggins a été employée pour calculer une limite supérieure pour les paramètres d'inter-actions; elle se situe de 2.6 à 4.7. Les isothermes peuvent être fixés de χ_1 la meilleure façon au moyen d'une équation modifiée de la loi d'Henry (voir le Synopsis). On discute de la signification possible des paramètres k, β et S_{max}.

Zusammenfassung

Die Wassersorptionsisotherme wurde für sechs Kautschukbinder, wie sie in festen Treibstoffen benützt werden, bei Raumtemperatur gemessen. Die Sättigungslöslichkeit lag bei 0,003 bis 0,030 g Wasser pro g Binder. Zur Berechnung eines oberen Grenzwerts für den Wechselwirkungsparameter χ_1 wurde die Flory-Huggins-Gleichung benützt. Diese Grenzwerte lagen bei 2,6 bis 4,7. Die Isotherme konnte am besten durch eine modifizierte Gleichung entsprechend dem Henry-Gesetz wiedergegeben werden (siehe engl. Zusammenfassung). Die mögliche Bedeutung der Parameter k, α, β und S_{max} wird diskutiert.