

## **Chemical-Physical Property Relationships for Asphalt Cements and the Dispersed Polar Fluid Model**

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### **Introduction**

A comprehensive, quantitative model relating chemical compositional parameters to the physical properties of asphalt cement is needed in order to optimize the production and modifications of asphalt cements in terms of costs and potential pavement performance. The chemical-physical property relationships presented in this paper, although only semi-empirical in nature, represent a significant step towards the achievement of this goal.

This paper presents the results of research carried out under the auspices of the Strategic Highway Research Program (SHRP), on the chemical and physical properties of asphalt cement and the development of performance-related specifications for asphalt binders. The body of the paper discusses the materials and equipment used in the rheological characterization of the asphalts studied, and then presents a mathematical model for describing the linear viscoelastic behavior of asphalt binders. A series of empirical chemical-physical property relationships are then presented, relating various chemical compositional parameters to the viscoelastic model parameters. The significance of these empirical relationships are then discussed within the context of the dispersed polar fluid (DPF) model for asphalt microstructure, previously proposed by the authors as a more appropriate molecular structure for explaining the mechanical behavior of commonly used asphalt binders, as compared to the traditional micellar or colloidal model (1).

### **The Dispersed Polar Fluid Model**

The DPF model is a conceptual model of the molecular structure of paving grade asphalt binders (1). It is an alternative to the traditional colloidal or micellar model. The most important difference between these two models is that the DPF model considers asphalt binders to be essentially single-phase systems, whereas colloidal models presume that there are two phases present, a continuous, low-polar phase, and a dispersed highly polar phase. In the traditional model, the dispersed phase is approximately represented by asphaltenes (2,3). According to the proposed DPF model, the mechanical properties of asphalt cement are dependent not upon the relative abundance of dispersed and continuous phases, but upon the magnitude and dispersion in both molecular weights and intermolecular forces (1). The DPF model applies only to paving asphalts currently in use. The authors do consider it is possible that certain asphalt binders, having very high concentration of polar molecules, may

be prone to phase separation, in which case a colloidal treatment of the microstructure would be entirely appropriate. It is however the authors' belief that the vast majority of asphalt binders now in use are best treated as single-phase systems.

## Materials and Methods

The asphalt cements used in this research are those included in the Materials Reference Library (MRL) established for execution of various SHRP research projects. A total of 17 asphalts were included for study in the research presented in this paper.

Dynamic mechanical analysis was performed on these asphalts using a Rheometrics Mechanical Spectrometer, model RMS-803. In this type of characterization, the linear viscoelastic properties of asphalt cements are characterized by determination of the complex modulus ( $G^*$ ) and the phase angle ( $\delta$ ) as a function of frequency. In this research, the frequencies used ranged from 0.1 to 100 rad/s, at temperatures ranging from -35 to 60 °C. Time-temperature superposition was used to construct master curves of  $G^*$  and  $\delta$ , and to construct the associated plots of the shift factor ( $a(T)$ ) as a function of temperature (4).

Use has been made in this research of various chemical data available in the SHRP database. These include Corbett fraction data and number average molecular weights determined by vapor pressure osmosis in toluene at 60 °C. These data are summarized in Table 1.

## Results

The mechanical response of viscoelastic materials such as asphalt cement is generally both time (frequency) and temperature dependent. In order to mathematically describe the linear viscoelastic behavior of asphalt cement, it is necessary to separate these effects, and model them as independent phenomena.

The frequency dependence of the linear viscoelastic response of asphalt cement can be mathematically modeled using the following series of equations. For characterizing the complex modulus as a function of frequency:

$$G^* = G_g \left[ 1 + \left( \frac{\omega}{\omega_c} \right)^{\frac{\log 2}{R}} \right]^{\frac{R}{\log 2}} \quad 1)$$

where:

- $G^*$  = complex dynamic modulus, in Pa, at frequency  $\omega$ , rad/s
- $G_g$  = glassy modulus, typically 1 GPa

$\omega_c$  = the crossover frequency, rad/s  
 R = the rheological index

A similar equation can be used to predict the phase angle, which is not presented here in the interest of brevity. The temperature dependence at high temperatures can be modeled using the well known Williams-Landel-Ferry (WLF) equation:

$$\log a(T) = \frac{-19(T-T_d)}{(92+T-T_d)} \quad 2)$$

where:

$a(T)$  = shift factor at temperature T (T in °C)  
 $T_d$  = the defining temperature, °C

At low temperatures, below  $T_d$ , an Arrhenius function is used to characterize the shift factors:

$$\log a(T) = \frac{H_a}{2.303R} \left[ \frac{1}{T} - \frac{1}{T_d} \right] \quad 3)$$

where:

$H_a$  = flow activation energy, 250 kJ/mol for paving grade asphalts  
 R = ideal gas constant, 8.314 kJ/mol·°K

In applying equations 1 through 3, the frequency  $\omega$  in equation 1 must be shifted relative to the selected reference temperature, which in this analysis has been chosen as  $T_d$ . This shifting simply involves multiplying the actual frequency at temperature T by the shift factor  $a(T)$ . Additionally, the crossover frequency,  $\omega_c$ , must be shifted to the reference temperature.

Another parameter of interest in evaluating the viscoelastic response of asphalt cements is the steady state viscosity,  $\eta_0$ . This represents the coefficient of newtonian viscosity, and is directly proportional to the resistance to flow under linear conditions.

Some explanation of the meaning of the various linear viscoelastic model parameters is in order at this point. The glassy modulus  $G_g$  represents the limiting complex modulus for a given asphalt cement, obtained at low temperatures and/or high frequencies. It is generally very close to  $10^9$  Pa for most asphalts; in the chemical-physical models presented below,  $G_g$  was assumed to be  $10^9$  Pa. The crossover frequency  $\omega_c$  represents the frequency at which  $\tan \delta$  is equal to one. It is called the crossover frequency because at this point, the storage ( $G' = G^* \cos \delta$ ) and loss moduli ( $G'' = G^* \sin \delta$ ) are equal; at higher frequencies, the loss modulus will be lower than the storage modulus, and at lower frequencies, the storage modulus is the lower. Therefore,  $\omega_c$  represents the point where  $G'$  and  $G''$  "crossover." The crossover frequency can be physically interpreted as representing the hardness of an asphalt;

higher values of  $\omega_c$  are indicative of harder asphalt binders, with greater resistance to flow. The steady-state viscosity  $\eta_0$ , as mentioned above, simply represents the coefficient of viscosity under linear flow conditions. This parameter and the crossover frequency are closely related. The rheological index  $R$  is proportional to the broadness of the relaxation spectrum. As the relaxation processes of an asphalt become more disperse, the value of  $R$  will increase, and the transition from glassy to viscous behavior becomes more gradual. Typically, pitch type asphalts will have a low value of  $R$  (approaching 1), whereas highly oxidized asphalts will have higher values, approaching or exceeding 3. The rheological index is numerically equivalent to the log of the ratio of the glassy modulus to the complex modulus at the crossover frequency. The meaning of these various parameters are graphically indicated in Figure 1, which depicts a typical plot of  $G^*$  versus  $\omega$  for a paving grade asphalt binder. The values of these parameters for the asphalts used in this research are given in Table 2.

The defining temperature,  $T_d$ , is a parameter characteristic of the temperature dependency of a selected asphalt. The value of  $T_d$  ranges from about -20 to 0 °C for commonly used asphalts, and is thus in the same range as the glass transition. As the defining temperature increases, the change in the shift factor with respect to temperature becomes greater, indicating an increase in temperature dependency. This is shown in Figure 2, which shows a plot of the shift factors calculated from equations 1 and 2, using  $T_d$  values of -20 and 0 °C. The defining temperature can be thought of as analogous to, or closely related to, the glass transition temperature. The authors however consider the glass transition to be a somewhat nebulous and controversial concept; if it exists for asphalt cements, it is certainly quite broad and poorly defined. Therefore, we suggest the use of the term "defining temperature," meaning a characteristic temperature which defines the temperature dependence of an asphalt, and which, as will be pointed out in the discussion, represents an approximately equivalent rheological point for comparison of the flow properties of asphalt cements.

Taken together, equations 1 through 3 allow the calculation of the complex modulus over a wide range of temperatures and frequencies. From such information, rational evaluation of the potential performance of an asphalt can be made, based upon its predicted mechanical response. These equations are generally valid at low to intermediate temperatures. At high temperatures, as viscous flow is approached, modifications are needed, which in the interest of brevity, are not presented here.

## Chemical-Physical Property Relationships

According to the DPF model, asphalt cement should be considered to be a single phase system, though exceedingly complex in composition and interactions among chemical species. The temperature dependence is primarily controlled by free volume effects; increasing temperature results in an increase in free volume among the constituent molecules, which increases molecular mobility and decreases resistance to flow (5). According to the proposed theory, the time dependence of asphalt cements is a function of the overall strength of molecular interactions, and the distribution in strengths of these interactions.

In developing chemical-physical property relationships, use was made of Corbett fraction data and number average molecular weights. Although these particular data should not be considered optimal for developing chemical-physical property relationships within the framework of the DPF model, they are adequate. Additionally, these are the only useful data available on all the SHRP asphalts at this time. Various linear regression models were proposed and evaluated, in which the rheological model parameters were predicted from one or two chemical parameters. Only those models which could be physically interpreted were considered. From this analysis, a series of empirical equations have been developed which can be used to predict the linear viscoelastic model parameters, and thus the stress-strain response, for a given asphalt cement. These equations are presented below.

For predicting the defining temperature, the following relationship was found ( $r^2 = 0.53$ , adjusted for degrees of freedom):

$$T_d = 16 - 0.57A - \frac{12,400}{M_n} \quad 4)$$

where:

A = asphaltene content (n-heptane), weight percent  
 $M_n$  = number average molecular weight, from VPO in toluene at 60 °C, Daltons

The following empirical equation was found to provide the best prediction of the crossover frequency  $\omega_c$  at the defining temperature,  $T_d$  ( $R^2 = 0.47$ , adjusted for degrees of freedom):

$$\log \omega_c(T_d) = -0.79 - 0.055A \quad 5)$$

The equation developed for estimating the rheological index R from the chemical data is as follows ( $r^2 = 0.81$ , adjusted for degrees of freedom):

$$R = -0.49 + 0.0018M_n + 1.90 \frac{(A+S)}{(P+N)} \quad 6)$$

where

S = saturate content, weight percent  
P = polar aromatic content, weight percent  
N = naphthene aromatic content, weight percent

Measured and predicted values of R are compared graphically in Figure 3.

The final model presented here, for predicting the steady-state viscosity at the defining temperature  $\eta_0(T_d)$ , is given below ( $r^2 = 0.71$ , adjusted for degrees of freedom):

$$\log \eta_0(T_d) = 7.42 + 0.094 A + 0.036 P$$

7)

Predicted values of the steady-state viscosity are plotted against measured values in Figure 4.

In estimating the linear viscoelastic response of a selected asphalt using these equations, the various rheological model parameters are first estimated from the empirical chemical-physical property relationship. Then, equations 1 through 3 can be used to predict the dynamic mechanical response at any given temperature. To provide an indication of the overall accuracy of these models, Figure 5 is presented, in measured values of  $G^*$  at 10 rad/s, for various temperatures, are plotted against predicted values. The agreement is within about a factor of two, which although not suitable for engineering design purposes, is certainly useful for a semi-quantitative evaluation of the effect of chemical compositional variables on the mechanical behavior of asphalts. A similar plot is shown as Figure 6, where measured and predicted shift factors are compared. The agreement between measured and predicted values is similar to that seen for  $G^*$ . Predicted modulus values can be used to predict the potential performance of a given asphalt cement. For example, these equations can be used to estimate the limiting stiffness temperature, which represents the temperature at which at given stiffness is achieved at a selected loading time. This limiting stiffness temperature then represents the predicted cracking temperature for a pavement made with the given asphalt cement (4).

## Discussion

The observed dependence of  $T_d$  on asphaltene content and molecular weight (equation 4), can be explained using the concept of free volume. The WLF equation can itself be derived from free volume considerations; from this sort of analysis, it can be shown that for a given form of the WLF equation, and assuming similar coefficients of thermal expansion above and below the glass transition, the reference temperature ( $T_d$  in this case) will approximately represent a point of equal free volume for a given family of materials (5). Therefore, for asphalt binders, factors which tend to increase free volume will decrease  $T_d$ , whereas factors which act to decrease free volume will increase  $T_d$ . For most viscoelastic systems, an increase in molecular weight will decrease free volume, which explains the observed dependence of  $T_d$  on the number average molecular weight. The observed decrease in  $T_d$  with increasing asphaltene content at first may seem contradictory. This however can be justified if it is assumed that increasing concentration of polar functions groups, rather than resulting in a net attraction among constituent molecules, results in a net repulsive force. This would tend to increase free volume, thus resulting in a higher defining temperature. The assumption of a net repulsive force among polar molecules is reasonable, since this is required for a stable dispersion (6). However, if the concentration of highly polar species is increased to the point of phase separation, a net attractive force would then exist. This should be expected to increase  $T_d$ , resulting in both a harder asphalt and an increase in temperature dependency. This may in fact explain the observed rapid failure of pavements constructed with asphalt cements having high asphaltene contents (6,7).

In developing the empirical relationships for the crossover frequency and the steady-state viscosity, both parameters were defined with  $T_d$  as the reference temperature. The discussion above concerning the effects of free volume should make the reason for this apparent to the reader. Since resistance to flow is so highly dependent on molecular mobility, and hence free volume, relating parameters such as  $\omega_c$  and  $\eta_0$  at random free volume states is pointless. By defining these parameters at  $T_d$ , which represents an approximately equivalent point of free volume, these effects are reduced or eliminated. The major factor effecting resistance to flow under such equal free volume states will then be intermolecular friction (5). From both equation 5 and equation 7, it is clear that resistance to flow for asphalt cements, at equal free volume, increases directly with increasing concentration of highly polar molecules. This is an obvious result of the increased intermolecular friction resulting from greater concentration of highly polar function groups within an asphalt.

The empirical model for estimating the rheological index  $R$  from molecular weight and Corbett data can be explained as follows. From consideration of various molecular models for viscoelastic materials, it can be deduced that the complex modulus at  $\tan \delta = 1$  should decrease with increasing molecular weight. Additionally, data on the molecular weight distribution of asphalt cements suggests that higher molecular weights are normally consistent with broader molecular weight distributions, which would also tend to decrease the modulus at the crossover point (8). As  $G^*$  at the crossover decreases,  $R$  will increase; thus, the observed increase in  $R$  with increasing molecular weight. The second term in equation 5 is a parameter suggested by the authors as being indicative of the dispersion in dipole strengths among an asphalt cements constituent molecules. This parameter, consisting of the sum of the asphaltenes and saturates, divided by the sum of the naphthene and polar aromatic fractions, represents the ratio of the very strongly polar and non-polar fractions of the asphalt, divided by the fractions of intermediate polarity. As this parameter increases, the dispersion in the polar forces within an asphalt should increase. Increased dispersion in such intermolecular forces, according to the DPF model, should produce a broader relaxation spectrum, and hence a higher rheological index. This is in fact supported by the form of equation 5.

Although the above series of equations is empirical, each of these equations is based on clear assumptions about the nature of the molecular sources of viscoelastic behavior in asphalt binders. These assumptions stem from the primary hypotheses of the dispersed polar fluid model. In some cases, such as with the use of the Corbett fraction data in predicting viscosity and rheologic type, alternate explanations could be made using the standard colloidal model of asphalt. Therefore, the construction of the quantitative model for chemical-physical property relationships is unfortunately not irrefutable proof of the validity of the DPF model. However, the construction of the chemical-physical property model presented here was made possible only by discarding many of the aspects of the traditional colloidal theory of asphalt microstructure, and replacing them with concepts based upon a single-phased, though complex, model of molecular structure.

## Conclusions

1. The temperature dependence of asphalt cements can be effectively explained using free volume concepts; increasing molecular weights decrease free volume, resulting in an increase in temperature dependency, whereas increasing polarity increases free volume, having the opposite effect.
2. Increasing amounts of highly polar material increase intermolecular friction in asphalt cements, increasing resistance to flow and overall hardness. This relationship can only be analyzed for a wide range of systems by comparison at a point of equal free volume, such as the defining temperature.
3. The rheologic type of an asphalt, or relaxation spectrum width, increases with increasing molecular weight and with increased dispersion in the strength of polar functional groups among constituent molecules.
4. The above relationships have been empirically quantified, and can be used in conjunction with a mathematical model to predict the linear viscoelastic response of a wide range of asphalts using chemical compositional parameters.
5. The results of this research lend significant support to the primary aspects of the dispersed polar fluid model of asphalt microstructure.

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Table 1. Corbett Fraction Data and Molecular Weights.

Asphalt	Asphaltene Content Wt. %	Polar Aromatics Wt. %	Napthene Aromatics Wt. %	Saturates Wt. %	M <sub>n</sub> Daltons
AAA-1	18.3	37.3	31.8	10.6	790
AAB-1	18.2	38.3	33.4	8.6	840
AAC-1	11.0	37.4	37.1	12.9	870
AAD-1	23.0	41.3	25.1	8.6	700
AAE-1	22.9	30.5	31.6	12.7	820
AAF-1	14.1	38.3	37.7	9.6	840
AAG-1	5.8	51.2	32.5	8.5	710
AAJ-1	10.6	41.5	35.9	10.9	1030
AAK-1	21.1	41.8	30.0	5.1	860
AAL-1	18.9	37.3	30.3	12.1	760
AAM-1	3.9	50.3	41.9	1.9	1300
AAN-1	15.7	33.9	40.1	10.3	890
AAO-1	16.4	32.9	41.8	8.6	930
AAP-1	12.6	36.9	36.4	13.2	1090
AAQ-1	16.2	25.9	44.8	12.5	810
AAR-1	18.4	30.5	41.1	10.0	880
AAS-1	18.3	34.1	39.7	5.9	960
AAT-1	17.3	42.5	32.3	7.7	880
AAU-1	17.7	40.5	33.6	7.9	880
AAV-1	9.2	39.5	38.9	10.9	890
AAW-1	17.9	35.7	37.1	9.3	890
AAX-1	11.9	41.3	39.6	7.9	970
AAZ-1	22.4	31.4	35.4	9.4	860
AAZ-1	8.9	42.0	43.1	6.8	970

Table 2. Linear Viscoelastic Model Parameters.

Asphalt	$T_d$ °C	Log $\omega_c$ at $T_d$ rad/s	R	$\eta_0$ at $T_d$ Pa-s
AAA-1	-19.3	-2.03	1.50	10.98
AAB-1	-11.6	-1.97	1.76	10.57
AAC-1	-5.5	-1.16	1.63	9.82
AAD-1	-17.1	-2.01	1.66	11.05
AAE-1	-10.4	-1.98	2.11	10.60
AAF-1	-7.0	-2.07	1.60	10.50
AAG-1	-3.9	-1.43	1.24	9.95
AAJ-1	-4.7	-1.67	1.90	10.00
AAK-1	-14.7	-2.33	1.60	11.31
AAL-1	-15.7	-1.28	1.61	10.37
AAM-1	1.0	-1.26	1.93	9.60
AAN-1	-5.4	-1.32	1.68	10.09
AAO-1	-10.1	-1.78	1.66	10.33
AAP-1	-5.1	-1.77	2.14	10.14
AAQ-1	-5.6	-1.46	1.66	9.94
AAR-1	-5.3	-1.54	1.89	10.08
AAS-1	-9.5	-1.93	1.79	10.49
AAT-1	-5.8	-1.96	1.72	10.50
AAU-1	-3.9	-1.34	1.72	9.94
AAV-1	-5.4	-0.93	1.53	9.60
AAW-1	0.0	-1.50	1.97	9.97
AAX-1	-0.9	-1.24	1.66	9.85
AAZ-1	-8.5	-2.07	2.04	10.62
AAZ-1	-1.0	-1.09	1.44	9.52

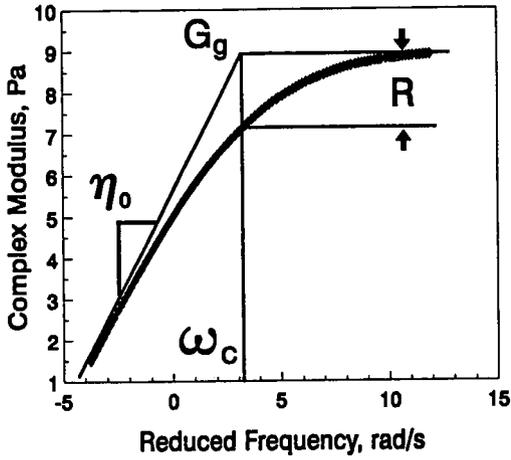


Figure 1. Typical master curve for asphalt binder, showing meaning of model parameters.

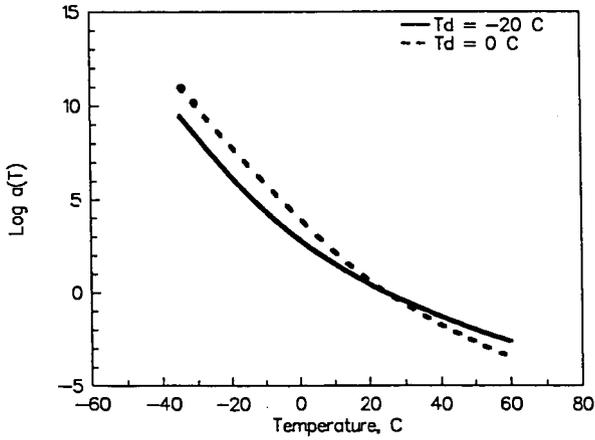
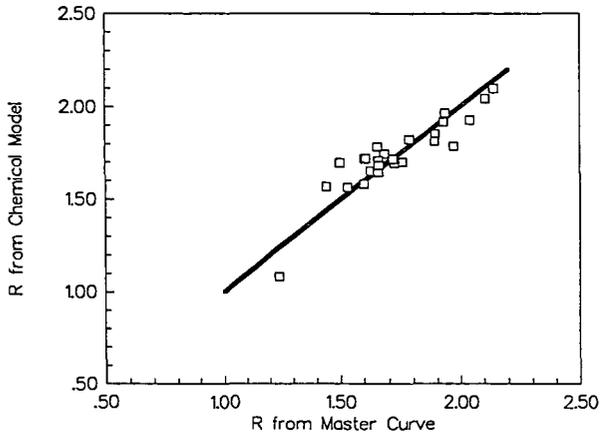
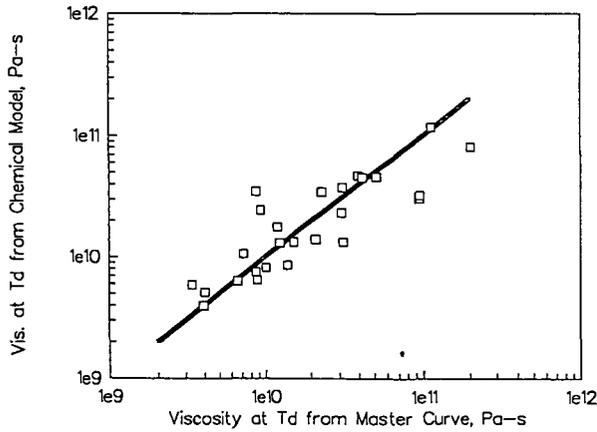


Figure 2. Shift factors as a function of temperature, for different  $T_d$  values.



**Figure 3.** Values of the rheological index,  $R$ , as predicted from chemical-physical model and determined from analysis of dynamic shear data.



**Figure 4.** Values of  $\eta_0$  at the defining temperature predicted from chemical-physical model, and as determined from analysis of dynamic shear data.

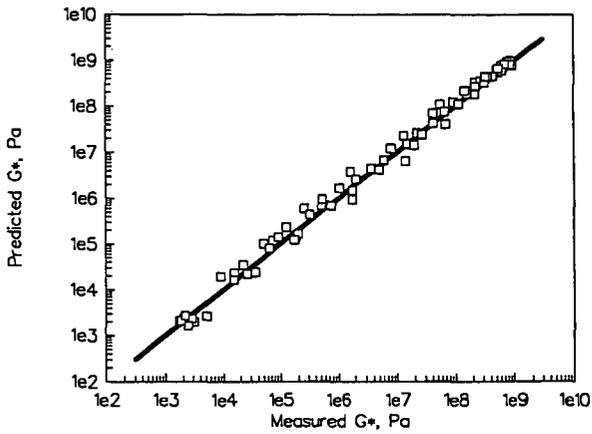


Figure 5. Comparison of predicted and measured values of the complex modulus,  $G^*$ , at 10 rad/s and at various temperatures.

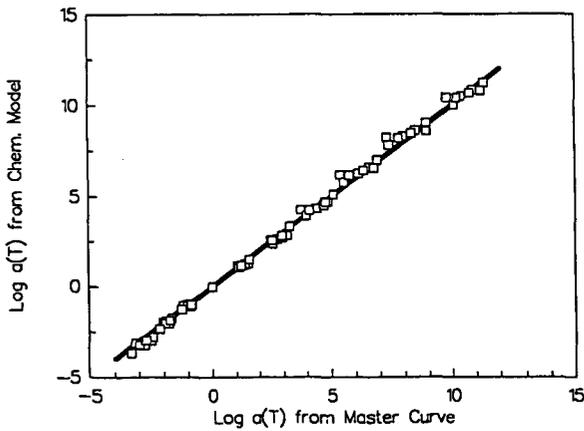


Figure 6. Predicted and measured values of  $\log a(T)$ .