

An Evaluation of the DAWN-B Light Scattering Unit from Wyatt Technology: Suggested Calibration, Normalization, and Clarification Procedures

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SYNOPSIS

Proper normalization, calibration, and sample clarification procedures for use with the Wyatt Technology DAWN-B laser light scattering photometer are described. The utility of the proposed methods is confirmed by comparing results obtained on the solution properties of polystyrene standards in three different solvents (toluene, tetrahydrofuran, and methyl ethyl ketone) with results from the literature and generated using a Chromatix KMX-6 low-angle light scattering photometer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Over the past several years, the DAWN-B light scattering instrument from Wyatt Technology has become widely used in polymer characterization. This unit features a "batch" cylindrical cell. The DAWN-F unit, with a flow-through cell design allowing coupling to size exclusion chromatography, is also being broadly utilized. These instruments offer potential advantages of simplicity and rapidity with the use of 15 fixed detectors that allow simultaneous measurement of scattered light intensity as a function of angle θ and computer interfacing for data accumulation and manipulation. These advantages are particularly appealing to scientists in industrial laboratories, who frequently are called upon to rapidly characterize many polymer samples.

The advantages of the DAWN units are achieved at a cost. Specifically, no measure of the intensity of the laser light transmitted directly through the sample ("incident intensity") is possible so calibration is required. The gain of each detector is different so normalization is necessary. Normalization is done through use of a small Rayleigh scatterer, where no angular dependence of the product $I(\theta) \cdot \sin \theta$, where

$I(\theta)$ is the intensity at the various scattering angles, is expected. Thus, the product $I(\theta) \cdot \sin \theta$ at all angles is adjusted to be the same as that measured at $\theta = 90^\circ$. Furthermore, with the DAWN-B unit adequate sample clarification can be difficult because of the large scattering volume and, unless expensive premium quality scattering cells are used, anomalous results may be obtained on changing cells to facilitate measurements at different concentrations.

In this article, we present procedures that address these problems. Results obtained for the weight-average molecular weight \bar{M}_w , radius of gyration R_g , and second virial coefficient A_2 of narrow molecular weight distribution polystyrenes in three different solvents are presented. These findings are compared with data obtained using the well-established Chromatix KMX-6 low-angle laser light scattering (LALLS) photometer and with literature data.

EXPERIMENTAL

Materials

Polystyrene standards were purchased from Pressure Chemical Company. The manufacturer's specifications and lot numbers for these materials are presented in Table I. Toluene and methyl ethyl ketone (MEK) were of ACS Certified grade from Fisher Scientific Co. Tetrahydrofuran (THF) was

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reagent grade from Aldrich. MEK and THF were stored over fresh 4 Å molecular sieves before use.

Instrumentation and Methods

The DAWN-B unit has 15 detectors mounted over a fixed angular range of about 23–128°. The light source was a vertically polarized He-Ne laser operating at wavelength $\lambda = 632.8$ nm. No control of temperature was possible with our instrumental configuration, thus all measurements correspond to a room temperature of about 22°C. The instrument was modified slightly to allow use of a closed-loop filtration system^{1,2} for solvent and solution clarification. This involved machining a new cover for the sample compartment to facilitate inlet and outlet tubes. Details of the closed-loop systems we used are given below. Gelman Acrodisc-CR poly(tetrafluoroethylene) filters with 0.2 μm porosity were employed.

Normalization was conducted using a solution of 4,000 molecular weight polystyrene in MEK. Calibration involved use of the 590,000 molecular weight polystyrene in toluene. Additional details of normalization and calibration are given below. All data were treated using conventional Zimm plots.³

LALLS experiments were conducted at room temperature using the Chromatix KMX-6 unit at 632.8 nm. The 6–7° annulus and 0.3-mm field stop were used. This instrument requires no calibration since incident intensity is measurable by use of a series of calibrated attenuators. \bar{M}_w and A_2 are derived from the equation

$$\frac{K_c}{R_\theta} = \frac{1}{M_w} + 2A_2c \quad (1)$$

where $K = [4\pi^2/(N_A\lambda^4)]n_0^2 (dn/dc)^2$, N_A is Avogadro's number, n_0 is the solvent refractive index, dn/dc is the specific refractive index increment, c

is concentration, and R_θ is the excess Rayleigh ratio. A closed loop system was again used for clarification purposes.

The dn/dc value for polystyrene in toluene at 632.8 nm and 22°C was measured as 0.109 mL g⁻¹ using the Otsuka DRM-1020 double beam differential refractometer. The dn/dc values in THF and MEK of, respectively, 0.188 and 0.212 mL g⁻¹ were taken from the literature.⁴ Values of n_0 were taken from Riddick, Bunger, and Sakano.⁵

RESULTS AND DISCUSSION

Initial attempts to employ the DAWN-B unit in our laboratories did not result in generation of coherent Zimm plots for well-defined linear polystyrene standards in toluene. Early in our work, we observed that the quality of the cells (actually flat-bottom scintillation vials from Wheaton Co.) supplied by Wyatt Technology was less than optimal, that is, the measured scattering intensity at a given angle changed when cells were changed or when a given cell was rotated in the holder. To overcome this problem, we decided to utilize a closed loop filtration system.^{1,2} This system allows for thorough removal of dust from polymer solutions and eliminates the need to change cells or alter the cell position during a series of measurements. The system involves attachment of inlet and outlet tubes to the cell; this is conveniently done using a solvent resistant rubber stopper and two stainless steel tubes. A peristaltic or other low-volume, leak-free pump is utilized to pump liquid from a glass reservoir, through a membrane filter, into the cell, and back to the reservoir (Fig. 1). For a series of measurements, a known volume of solvent is cleaned, measurements are made, a known volume of stock solution is added to the reservoir and circulated until constant scattering intensity is observed, measurements are again made, etc. To facilitate the inlet and outlet tubes going to and from the cell, a new cover with small openings was machined from aluminum and painted black (to minimize reflections) using solvent-resistant paint.

Normalization was the next problem to be addressed. The DAWN-B manual suggests using toluene as the isotropic scatterer, but in our experience this is not practical because of the very weak scattering signal of toluene. Kim and Cotts,⁶ in an excellent paper that compares results obtained using several currently available light scattering instruments both in static modes and on-line with size exclusion chromatography, utilized polystyrene of

Table I Molecular Characteristics of Polystyrene Standards

Lot Number	M_w	\bar{M}_w/\bar{M}_n^a
50124	233,000	1.06
30121	590,000	1.06
80323	900,000	1.10
61111	2,000,000	1.30

Values from Pressure Chemical Co. Nominal values from supplier.

^a Maximum values. \bar{M}_n is the number-average molecular weight.

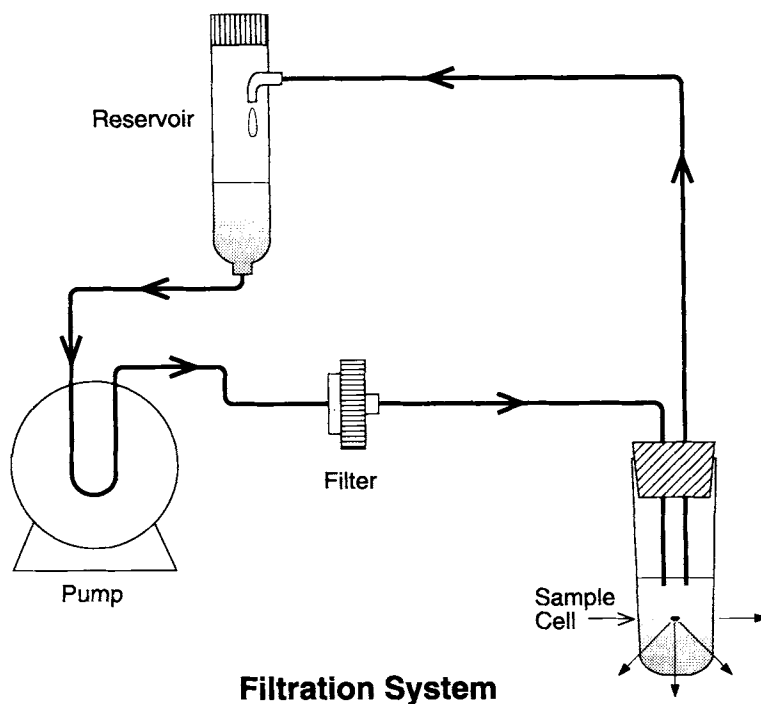


Figure 1 Schematic diagram of the closed loop system.

9,000 molecular weight in toluene to determine the normalization coefficients for the DAWN-F unit. When we utilized this same system for normalization of DAWN-B and then conducted R_g measurements, we repeatedly underestimated R_g by a small but con-

sistent amount. Even when we utilized a 5,800 M_w polystyrene, we also observed a small effect. We attempted to use a 2,000 M_w sample in toluene but very high concentrations were necessary to obtain adequate scattering intensities. Finally, we settled

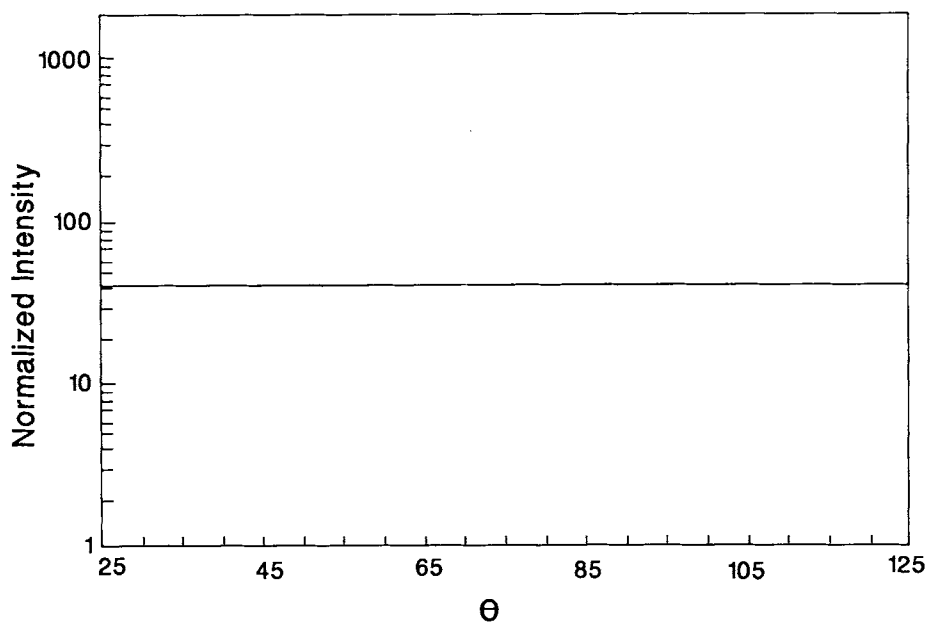


Figure 2 Normalization of the DAWN-B unit using polystyrene with $M_w = 4,000$ in MEK.

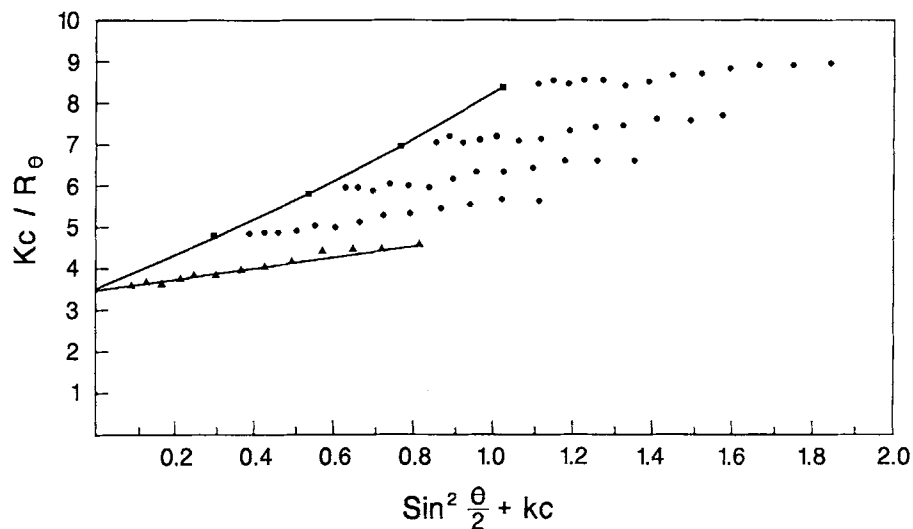


Figure 3 Zimm plot for a polystyrene of nominal molecular weight of 900,000 in toluene.

on using a 4,000 M_w polystyrene sample in MEK as the normalization system. The choice of MEK as solvent has two advantages: polystyrene chains are smaller in MEK than in toluene and, more importantly, the dn/dc value (0.212 mL g^{-1}) is very large resulting in adequate scattering levels at about 3% concentration. A typical normalization plot is shown in Figure 2. Once the instrument is normalized with a given cell, that cell should be cleaned and placed back into the holder in exactly the same position

(use marks on cell and holder). Anytime the cell is changed, normalization must be repeated; in our experience a single cell can be used for a long time (days or weeks) with no need to normalize again so long as the above precautions are taken. Mention is also made in the DAWN-B manual of using aqueous suspensions of polystyrene latices of 50 nm or less in radius as a normalization medium. Our experience would suggest that this approach should be viewed with caution.

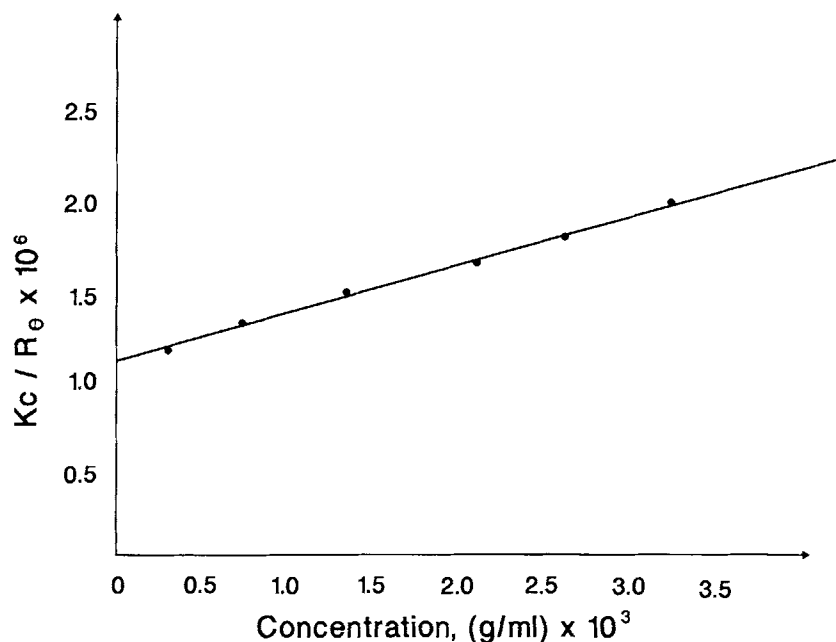


Figure 4 Results obtained using the KMX-6 LALLS unit in toluene for the $M_w = 900,000$ polystyrene of Figure 3.

Table II Summary of Light Scattering Results in Toluene

Lot No.	$\bar{M}_w \times 10^{-5}$		$A_2 \times 10^4$ (mL mol g ⁻²)			R_g (nm)	
	KMX-6	DAWN	KMX-6	DAWN	Lit. ^a	DAWN	Lit. ^b
50124	2.70	2.80	4.64	5.00	4.16	—	—
30121	5.90	5.90	3.90	3.95	3.37	33.7	33.0
80323	9.00	9.20	3.35	3.40	3.00	40.3	42.3
61111	19.5	19.6	2.99	3.05	2.43	67.0	66.5

^a From $A_2 = 1.25 \times 10^{-2} \bar{M}_w^{-0.272}$ (reference 7).

^b From $R_g = 1.37 \times 10^{-2} \bar{M}_w^{0.586}$ (reference 7).

Calibration was the final difficulty to be overcome. The DAWN-B manual suggests using two or more solvents of known Rayleigh ratio as calibrants. In our opinion, this approach is again plagued by the rather weak scattering of these solvents. We preferred to calibrate using a high molecular weight polystyrene standard of known (in this case 590,000) molecular weight. Such materials, which have been thoroughly and repeatedly characterized using various instruments, are kept in our laboratory for use as calibrants, usually for size exclusion chromatography. A coherent Zimm plot was first obtained and then from the mutual intercept of the plot, knowing \bar{M}_w , we could calculate the calibration constant. Using toluene as the solvent at room temperature we obtained a value of 1.550×10^{-3} for the calibration constant U_t . As long as toluene is used as solvent and as long as the voltage to the photomultiplier tube is constant, this value of U_t can be used. If the voltage changes by more than 1–2%, the calibration constant must be adjusted to correct for this effect.

The calibration constant is system dependent. From Zimm Plots of the same polystyrene sample (M_w of 590,000) in THF and MEK, we noticed that the calibration constants calculated (1.450×10^{-3} for THF and 1.430×10^{-3} for MEK, respectively) are relatively smaller than that in toluene. We also checked the PS/cyclohexane system and found that the following empirical formula is suitable to compute the calibration constants for different solvents used:

$$U_x = \frac{n_x}{n_t} \cdot U_t \quad (2)$$

where U_x is the calibration constant in the other solvent of refractive index n_x and n_t is the refractive index of toluene.

This refractive index dependence of the calibration constant may be attributable the fact that a change in refractive index results in corresponding changes of scattering geometry of the 15 perma-

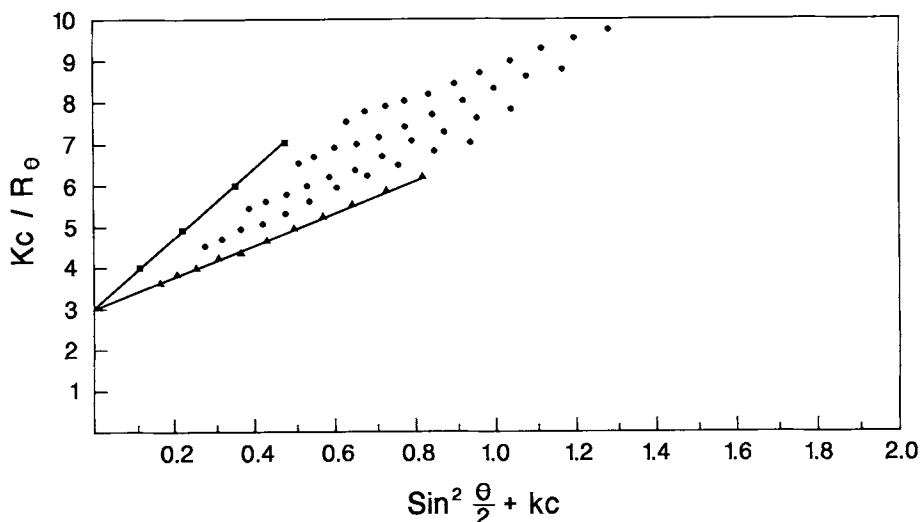


Figure 5 Zimm plot for a polystyrene of nominal molecular weight of 2×10^6 in THF.

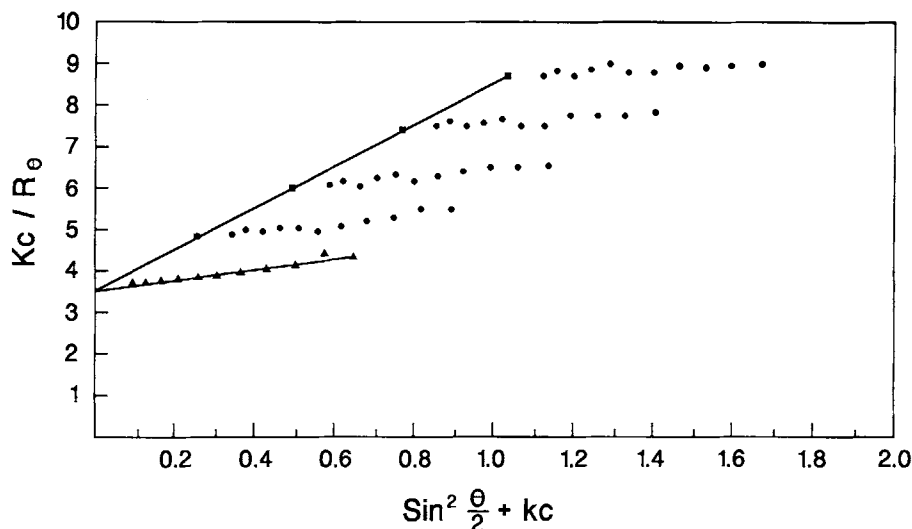


Figure 6 Zimm plot for a polystyrene of nominal molecular weight of 233,000 in MEK.

nently mounted detectors. In this way, we obtained for our instrument U_x values of 1.457×10^{-3} , 1.428×10^{-3} , and 1.479×10^{-3} for THF, MEK, and cyclohexane, respectively.

To examine the utility of our approach, we performed light scattering experiments on the four samples of Table I in toluene using both the DAWN-B and KMX-6 units. Representative plots of the data are shown in Figures 3 and 4. For the DAWN-B unit we consistently had to omit from consideration data obtained at the two lowest (and in some cases the third and fourth lowest) angles because these data exhibited anomalous behavior. Kim and Cotts⁶ also omitted data obtained at these smallest angles; this does not pose a problem for routine work.

Data obtained in toluene are presented in Table II. It is clear that excellent agreement exists between data for \bar{M}_w and A_2 values obtained with the two instruments. The findings for R_g and A_2 may also

be compared with literature data⁷ for the polystyrene/toluene system. The agreement between literature and measured R_g values is extremely good; agreement with literature A_2 results is also adequate if the larger experimental errors involved in measuring this parameter are considered.

Representative Zimm plots obtained in THF and MEK are presented in Figures 5 and 6. A comparison of our experimental results with A_2 and R_g values from the literature is given in Tables III and IV. For results in both THF and MEK there is good agreement with molecular weight results previously obtained in toluene (Table II). A_2 results also agree nicely with data available in the literature. With one exception the R_g results measured in THF agree with literature data, although it must be emphasized that R_g data in the literature for the polystyrene/THF system exhibit considerable scatter.⁹ Our values for R_g of two polystyrene samples in MEK are

Table III Results From DAWN-B for Polystyrene in THF

Lot No.	$\bar{M}_w \times 10^{-5}$		$A_2 \times 10^4$ (mL mol g ⁻²)		R_g (nm)	
	KMX-6 ^a	DAWN	DAWN	Lit. ^b	DAWN	Lit. ^c
50124	2.70	2.75	4.68	4.43	—	—
30121	5.90	5.94	4.06	3.65	26.1	34.4
80323	9.00	9.03	3.41	3.29	39.5	43.9
61111	19.5	20.7	3.01	2.72	68.5	68.7

^a Toluene system.

^b From $A_2 = 9.60 \times 10^{-3} \bar{M}_w^{-0.246}$ (reference 7).

^c From $R_g = 1.59 \times 10^{-2} \bar{M}_w^{0.578}$ (reference 7).

Table IV Results From DAWN-B for Polystyrene in MEK

Lot No.	$\bar{M}_w \times 10^{-5}$		$A_2 \times 10^4$ (mL mol g ⁻²)		R_g (nm)	
	KMX-6 ^a	DAWN	DAWN	Lit. ^b	DAWN	Lit. ^c
20124	2.70	2.80	1.25	1.22	—	—
30121	5.90	5.99	1.19	1.02	—	—
80323	9.00	8.90	0.86	0.92	29.2	34.7
61111	19.5	18.4	0.60	0.77	48.2	53.9

^a Toluene system.

^b From reference 8; at 22°C: $A_2 = 2.37 \times 10^{-3} \bar{M}_w^{-0.237}$.

^c From reference 9: $R_g = 1.40 \times 10^{-2} \bar{M}_w^{0.570}$.

slightly smaller than those reported by Park et al.,⁹ despite the good agreement observed between \bar{M}_w results for this and other systems and the agreement with literature values of A_2 .

In summary, we have described techniques that may be helpful in obtaining meaningful experimental results using the DAWN-B photometer. Results obtained thus far for polystyrene in toluene, THF, and MEK appear to support the utility of these procedures. With proper care, the DAWN-B instrument is capable of generating high quality static light scattering data. We also note that Wyatt Technology has very recently introduced a "magic glass" standard that can be used in normalization and calibration of the DAWN unit. The use of this known isotropic scattering standard, in principle, avoids some of the pitfalls that are addressed in this paper: the difficulty in solution and solvent clarification and the weak scattering signal from solvents that results in poor signal-to-noise ratio. In practice, proper calibration of these glass standards is essential if reliable results are to be obtained from their use.

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