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SOLUBILITY PARAMETERS OF POLY(α -METHYLSTYRENE-CO-ACRYLONITRILE) FROM GAS-LIQUID CHROMATOGRAPHY

K. S. SIOW* and S. H. GOH

Department of Chemistry, National University of Singapore, Kent Ridge, 0511 Singapore (Singapore)
and

K. S. YAP

Chemical Process Technology Department, Singapore Polytechnic, 0513 Singapore (Singapore)

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SUMMARY

Solubilities of fourteen polar and non-polar solvents in poly(α -methylstyrene-co-acrylonitrile) have been measured by the gas chromatographic method over the temperature range 165–195°C. The Flory–Huggins χ parameters, partial molar heats of mixing ($\Delta\bar{H}_1^\circ$) and heats of solution (ΔH_s) were calculated and the infinite-dilution solubility parameter (δ_2°) for the polymer was estimated following the method of Di Paola-Baranyi and Guillet. At 180°C (midpoint of the temperature range investigated), δ_2° was found to have a value of 8.0 (cal/ml)^{1/2}. By linear extrapolation, the χ parameter at 25°C was also estimated, which yielded a value of 9.9 for δ_2° at 25°C.

INTRODUCTION

Since the pioneering work of Smidsrød and Guillet¹, inverse gas chromatography has become a method of much use in polymer studies. It has been used to evaluate various properties of polymers, such as the melting and glass transition points, crystallinity, diffusion coefficient, and surface as well as thermodynamic properties. It has been generally established that thermodynamic data obtained from this method can be as reliable and accurate as those determined by the static methods. The practical requirements and proper procedure required to derive reliable thermodynamic data from such a method have been given by Young². A great advantage of the method is its speed, which makes it preferable to the time-consuming conventional methods.

In this paper we report the determination of solubility parameters of poly(α -methylstyrene-co-acrylonitrile), MSAN, by inverse gas chromatography. Studies on this polymer have been scarce and there is little information relating to its thermodynamic properties. This work is part of our continuing project to study the miscibility of MSAN with solvents of small molecules and with other polymers³.

EXPERIMENTAL

The MSAN polymer used was Luran KR 2556U, manufactured by BASF. It contains 30% (w/w) acrylonitrile and has a weight-average molecular weight M_w of 160 000. All solutes (the compounds to be injected into the column) were obtained from standard suppliers and were used without further purification.

The columns were prepared in the usual manner. The polymer was dissolved in 2-butanone and then deposited on Chromosorb G AW DMCS (60–80 mesh) by evaporation of the solvent. After vacuum drying for about 72 h with slight heating, the coated support was resieved and packed into 1/4-in. (O.D.) copper tubing. The exact loading of polymer on the support was determined by calcination using a suitable blank correction. To assure reproducibility, two columns were prepared with loadings of 8.01 and 8.78% (w/w), the weights of polymer in the columns being 1.493 and 1.277 g, respectively.

Chromatographic measurements were carried out on a Hewlett-Packard 5790 gas chromatograph equipped with a dual flame ionization detector. The apparatus, with a slight modification to facilitate measurement of column inlet pressure, can be operated with conditions meeting the requirements of Young. The carrier gas used in all measurements was nitrogen. Flow-rates chosen at *ca.* 20 ml/min were measured at the end of the column with a soap-bubble flow-meter. The column inlet pressure was measured with a mercury manometer, while the outlet pressure was always atmospheric. The oven temperature was measured to 0.01°C. Solute samples, mixed with a small amount of methane marker, were injected manually with a 10- μ l Hamilton syringe. To keep the sample size as small as possible, the solutes were usually injected in vapour form. In general, the solutes were characterized by symmetrical elution peaks, exhibiting sample size-independent retention volumes.

Data reduction followed standard procedures^{4,5}. The parameters of the solutes required were obtained as follows. Vapour pressures were calculated from the Antoine equation using the constants taken from standard sources^{6,7}. Second virial coefficients, B_{11} , were computed using the method of O'Connell and co-workers^{8,9}, except those for the hydrocarbons, which were calculated from the corresponding state equations of McGlashan and Potter¹⁰. Molar volumes, except those of *n*-dodecane and *n*-tetradecane¹¹, were calculated from the modified Rackett equations^{9,12}. The specific volumes of MSAN were estimated from the Simha-Boyer relation¹³.

RESULTS AND DISCUSSION

Fourteen solutes of differing molecular structures and polarities have been used in this study. Retention volumes were measured at 13 temperatures in the range 165–195°C. The temperatures are more than 50° above the T_g (115°C) of MSAN, a recommended condition for the thermodynamic study of polymers by the chromatographic method¹⁴.

Specific retention volumes were corrected to 0°C. The weight fraction activity coefficients and the χ parameters, derived from the specific retention volume results, are listed in Table I at selected temperatures. Both these quantities show, in all cases except dichloromethane, a decrease in their values with increasing temperature. This

TABLE I

THERMODYNAMIC INTERACTION PARAMETERS FOR VARIOUS SOLUTES IN MSAN

Solute	165°C		180°C		195°C	
	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ	$(a_1/w_1)^\infty$	χ
<i>n</i> -Dodecane	79.20	2.910	54.56	2.526	45.64	2.335
<i>n</i> -Tetradecane	82.39	2.978	60.73	2.664	50.81	2.476
Benzene	7.37	0.650	6.61	0.537	6.16	0.467
Toluene	8.09	0.745	7.27	0.624	7.16	0.602
<i>n</i> -Butylbenzene	11.08	1.066	9.70	0.923	9.13	0.851
Dichloromethane	4.54	0.577	4.52	0.577	4.64	0.608
Chloroform	4.41	0.671	4.01	0.576	3.90	0.551
Chlorobenzene	4.83	0.506	4.49	0.421	4.46	0.401
<i>n</i> -Butanol	10.71	0.932	9.13	0.768	8.29	0.673
Cyclohexanol	8.57	0.909	6.98	0.689	6.38	0.584
<i>n</i> -Butyl acetate	11.56	1.109	9.87	0.942	9.27	0.877
Dioxane	5.94	0.607	5.50	0.519	5.52	0.517
Tetrahydrofuran	8.04	0.752	6.65	0.562	6.59	0.556
2-Butanone	8.64	0.712	7.88	0.620	7.57	0.583

suggests that the solubilities of the solutes in MSAN increase with temperature. The largest activity coefficients and χ parameters are observed for the two *n*-alkanes, which are typical non-solvents for the polymer.

The partial molar heats of mixing ($\Delta\bar{H}_1^\infty$) and heats of solution (ΔH_s) for the solutes in MSAN are shown in Table II. Partial molar heats of mixing are given by

$$\Delta\bar{H}_1^\infty = R\partial\ln(a_1/w_1)^\infty/\partial(1/T) \quad (1)$$

TABLE II

PARTIAL MOLAR HEATS OF MIXING AND HEATS OF SOLUTION OF VARIOUS SOLUTES IN MSAN

Temperature range is 165–195°C.

Solute	$\Delta\bar{H}_1^\infty$ (kcal/mol)	$-\Delta H_s$ (kcal/mol)
<i>n</i> -Dodecane	7.49 ± 0.37	3.98 ± 0.35
<i>n</i> -Tetradecane	6.23 ± 0.26	7.16 ± 0.24
Benzene	2.02 ± 0.14	4.41 ± 0.14
Toluene	1.63 ± 0.20	5.63 ± 0.18
<i>n</i> -Butylbenzene	2.53 ± 0.15	7.31 ± 0.14
Dichloromethane	-0.60 ± 0.20	5.95 ± 0.20
Chloroform	1.77 ± 0.16	4.08 ± 0.15
Chlorobenzene	1.03 ± 0.12	6.96 ± 0.11
<i>n</i> -Butanol	3.84 ± 0.15	5.76 ± 0.13
Cyclohexanol	3.77 ± 0.24	6.16 ± 0.21
<i>n</i> -Butyl acetate	2.71 ± 0.22	5.24 ± 0.20
Dioxane	1.07 ± 0.20	6.18 ± 0.19
Tetrahydrofuran	2.79 ± 0.32	3.15 ± 0.31
2-Butanone	1.66 ± 0.12	4.80 ± 0.11

Heats of solution can be obtained in a similar manner from the temperature dependence of the specific retention volume

$$\Delta H_s = -R\delta(\ln V_g)/\partial(1/T) \quad (2)$$

The uncertainty limits in the table refer to the standard errors in the slope, as given by a linear least-squares analysis of the data. The values of ΔH_1° vary, in general, with the solutes in a manner consistent with that observed from the interaction parameters.

The polymer solubility parameter δ_2 was estimated in the manner described by Di Paola-Baranyi and Guillet¹⁵, from the following equation

$$\chi = (V_1/RT) (\delta_1 - \delta_2)^2 \quad (3)$$

Eqn. 3 can be rewritten

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right) \delta_1 - \frac{\delta_2^2}{RT} \quad (4)$$

and δ_2 can be obtained from plotting $(\delta_1^2/RT - \chi/V_1)$ against δ_1 . The required solubility parameters of the solutes (δ_1) can be evaluated from the definition

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \quad (5)$$

while ΔH_v , the heat of vaporization of solute, can be obtained directly from chromatographic data from the relation¹⁵

$$\Delta H_v = \Delta H_1^\circ - \Delta H_s \quad (6)$$

Values of δ_1 and ΔH_v so obtained at 180°C (midpoint of the temperature range investigated), as well as V_1 , the molar volumes of the solutes, are summarized in Table III. It has been found that the present ΔH_v values agree very well with the literature values available⁶. A plot of $(\delta_1^2/RT - \chi/V_1)$ against δ_1 at 180°C is shown in Fig. 1a. A straight line is obtained, as would be expected from eqn. 4, with a slope of $(2\delta_2/RT)$ and an intercept of $(-\delta_2^2/RT)$. A linear least-squares analysis gives 8.0 ± 0.2 and 8.2 ± 0.2 (cal/ml)^{1/2} from the slope and the intercept, respectively.

The variation of χ with temperature has been found to fit the following equation

$$\chi = \alpha + \beta/T \quad (7)$$

The constants α and β , determined from a linear least-squares analysis, are shown in Table IV. The linear correlation in most cases, except dichloromethane, is good. If such a relationship is assumed to extend to lower temperatures, values of χ at 25°C can be obtained by extrapolation. A value of δ_2 at 25°C can then be estimated as above (see Fig. 1b). The values of δ_2 so obtained are 9.9 ± 0.4 and 10 ± 0.4 (cal/ml)^{1/2} from the slope and the intercept, respectively. There are no literature values of δ_2 for MSAN for comparison. However, a value of 10.4 at 25°C has been estimated by

TABLE III

 V_1 , δ_1 AND ΔH_v VALUES FOR THE SOLUTES AT 180°C

Solute	V_1 (ml/mol)	ΔH_v kcal/mol	δ_1 (cal/ml) ^{1/2}
<i>n</i> -Dodecane	272.2	11.47 ± 0.72	6.23
<i>n</i> -Tetradecane	307.4	13.39 ± 0.50	6.37
Benzene	110.3	6.43 ± 0.28	7.08
Toluene	131.3	7.26 ± 0.38	6.96
<i>n</i> -Butylbenzene	189.4	9.84 ± 0.29	6.87
Dichloromethane	78.8	5.35 ± 0.40	7.51
Chloroform	98.4	5.85 ± 0.31	7.10
Chlorobenzene	121.3	7.99 ± 0.23	7.64
<i>n</i> -Butanol	114.8	9.24 ± 0.28	8.52
Cyclohexanol	128.4	9.93 ± 0.45	8.36
<i>n</i> -Butyl acetate	163.6	7.95 ± 0.42	6.57
Dioxane	105.6	7.25 ± 0.39	7.75
Tetrahydrofuran	100.0	5.94 ± 0.63	7.10
2-Butanone	111.8	6.46 ± 0.23	7.05

means of the Small method¹⁶, which should be able to provide some indication as to the validity of the present determination.

As has been noted in many earlier studies^{17,18}, the δ_2 values obtained from the intercept are slightly higher than those derived from the slope. Moreover, the χ parameters recalculated from eqn. 3, using the values of δ_2 obtained from the slope, are always lower than those observed. Table V shows the differences (γ) between such calculated and observed χ , and it is noted that the two *n*-alkanes appear to be rather odd, with γ values much larger than those for the others, which are more or less constant around an average of 0.54.

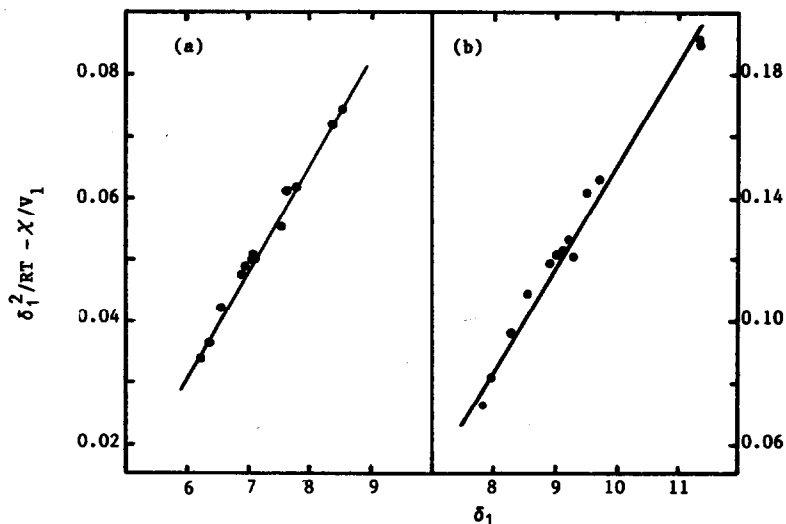
Fig. 1. Plot of $(\delta_1^2/RT - \chi/V_1)$ against δ_1 at (a) 180°C and (b) 25°C.

TABLE IV

TEMPERATURE DEPENDENCE OF THE χ PARAMETER OF VARIOUS SOLUTES IN MSANTemperature range is 165–195°C. The data were fitted to an equation of the form $\chi = \alpha + \frac{\beta}{T}$.

<i>Solute</i>	α	β	<i>Correlation coefficient</i>
<i>n</i> -Dodecane	-6.076	3915.5	0.9859
<i>n</i> -Tetradecane	-4.509	3260.0	0.9900
Benzene	-1.739	1038.1	0.9694
Toluene	-1.483	964.2	0.9296
<i>n</i> -Butylbenzene	-2.199	1418.5	0.9820
Dichloromethane	1.340	-346.2	0.6806
Chloroform	-1.194	807.8	0.9240
Chlorobenzene	-1.087	690.5	0.9549
<i>n</i> -Butanol	-3.163	1784.1	0.9859
Cyclohexanol	-3.921	2098.1	0.9796
<i>n</i> -Butyl acetate	-2.233	1449.3	0.9607
Dioxane	-0.923	656.8	0.8553
Tetrahydrofuran	-2.539	1426.8	0.9205
2-Butanone	-1.159	811.4	0.9631

Eqn. 3 is the original solubility parameter equation based on the Hildebrand–Scatchard and the Flory–Huggins theory. Huggins¹⁹ and also Scott and Magat^{20,21} deduced later that χ should be more properly expressed by

$$\chi = (V_1/RT) (\delta_1 - \delta_2)^2 + \gamma \quad (8)$$

TABLE V

COMPARISON OF OBSERVED AND CALCULATED χ PARAMETERS FOR VARIOUS SOLUTES IN MSAN

<i>Solute</i>	χ_{obs}	χ_{cal}	γ ($\chi_{obs} - \chi_{cal}$)	γ/V_1
<i>n</i> -Dodecane	2.526	0.95	1.58	0.0058
<i>n</i> -Tetradecane	2.664	0.91	1.75	0.0057
Benzene	0.537	0.10	0.44	0.0040
Toluene	0.624	0.16	0.46	0.0035
<i>n</i> -Butylbenzene	0.923	0.27	0.65	0.0034
Dichloromethane	0.577	0.02	0.56	0.0071
Chloroform	0.576	0.09	0.49	0.0050
Chlorobenzene	0.421	0.02	0.40	0.0033
<i>n</i> -Butanol	0.768	0.03	0.74	0.0064
Cyclohexanol	0.689	0.02	0.67	0.0052
<i>n</i> -Butyl acetate	0.942	0.37	0.57	0.0035
Dioxane	0.519	0.01	0.51	0.0048
Tetrahydrofuran	0.562	0.09	0.47	0.0047
2-Butanone	0.620	0.11	0.51	0.0046

* Calculated from $\chi = (V_1/RT) (\delta_1 - \delta_2)^2$, with $\delta_2 = 8.0$.

where γ is essentially an empirical parameter and could be considered as an entropy correction term. If this equation is used in place of eqn. 3, it will give, on rearrangement

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right) \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\gamma}{V_1}\right) \quad (9)$$

This shows that a plot of $(\delta_1^2/RT - \chi/V_1)$ against δ_1 will now give $(2\delta_2/RT)$ as the slope, but $-(\delta_2^2/RT + \gamma/V_1)$ instead of $-(\delta_2^2/RT)$ as the intercept. It follows then that the δ_2 values obtained from the slope of a plot of eqn. 4 should be the more accurate ones.

Table V also gives the γ/V_1 values for all the MSAN-solute systems. They are all about constant now, including those for the two n -alkane systems, with an average of 0.0048. Using this average γ/V_1 value and the value of δ_2 obtained from the slope of the plot of eqn. 4, the values of χ can be recalculated from

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 + \left(\frac{\gamma}{V_1}\right) V_1 \quad (10)$$

which are in good agreement with the observed χ values.

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