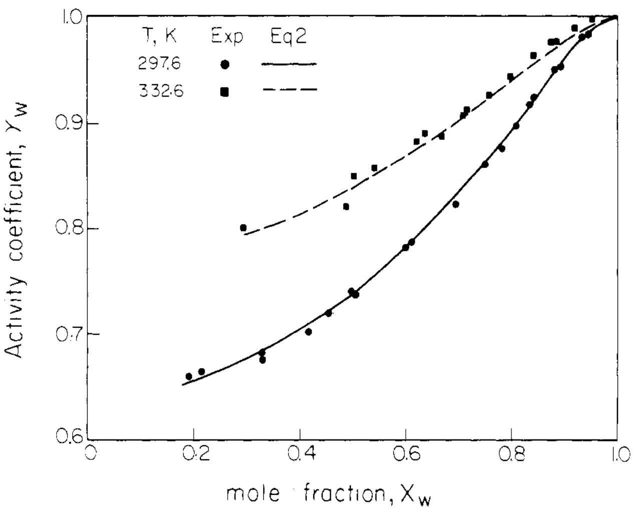

Figure 1. Activity coefficient of water as a function of its mole fraction.

Equilibrium values of the water mole fraction x_w in the triethylene glycol solution and the LiCl molalities at 297.6 and 332.6 K together with calculated values of ϕ_{LiCl} (Gibbard et al. (*6*)), a_w (eq 1), and the activity coefficient γ_w are listed in Table I. Insignificant amounts of triethylene glycol were transferred to the LiCl solutions. In Figure 1 the activity coefficients γ_w are plotted as a function of x_w. They are fitted to a Van Laar equation:

$$\ln \gamma_w = A_{12}/\left(1 + \frac{A_{12}}{A_{21}} \frac{x_w}{1 - x_w}\right)^2 \qquad (2)$$

where the constants A_{12} and A_{21} and the standard deviation of errors are given in Table II. The agreement between the predicted values from eq 2 and the experimental values is good, as shown in Figure 1.

Registry No. Water, 7732-18-5; triethylene glycol, 112-27-6.

Literature Cited

(1) "Glycols"; Union Carbide Corp.: New York, 1978.
(2) Fleischer, J. *Chem.-Ing.-Tech.* **1973**, *45*, 74-82.
(3) Jelinek, K.; Lesek, F.; Sivokova, M. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2650-6.
(4) Wise, H.; Puck, T. T.; Failey, C. F. *J. Phys. Chem.* **1950**, *54*, 734.
(5) Ishiguro, T.; Matsumoto, K. *J. Pharm. Soc. Jpn.* **1956**, *75*, 1414.
(6) Gibbard, H. F.; Scatchard, G. *J. Chem. Eng. Data* **1973**, *18*, 293.
(7) Gibbard, H. F.; Scatchard, G.; Rousseau, R. A.; Creek, J. L. *J. Chem. Eng. Data* **1974**, *19*, 281.

Received for review May 10, 1983. Accepted October 14, 1983.

Ultrasonic Velocity in Polystyrene-Toluene Solutions

Jeffrey C. Heine and William J. Snyder*
Chemical Engineering Department, Bucknell University, Lewisburg, Pennsylvania 17837

Sound velocities and densities of solutions of polystyrene (PS) and styrene in toluene were measured from 10 to 50 °C at 1 atm. Three polystyrene samples having molecular weights of 9100, 290 000, and 1 840 000 were used in this study. Concentrations ranged from 0 to 20 wt % polystyrene in toluene. Sound velocity measurements accurate to better than 1 m/s were made by using a MAPCO sonic solution monitor Model 6105 while solution densities were measured by using Lipkin and bottle pycnometers. Sound velocity of the polymer solutions was found to be independent of polystyrene molecular weight over the 0-10 wt % concentration range. However, the sound velocity-concentration relation for the styrene monomer was significantly different from that of the polymer. The sound velocity-concentration relationship for polystyrene solutions at 30 °C showed slight curvature between 0 and 19.75 wt % with values of 1279.2 and 1313.1 m/s, respectively.

Introduction

There is a need for accurate thermodynamic data on dilute polymer solutions for process control applications and elucidation of solution theory. An easily measurable thermodynamic property of liquids is sound velocity. It has been demonstrated that sound velocity can be used to determine many physicochemical properties of organics (*1*,*2*). The use of sound velocity to study polymer solutions, however, has been somewhat limited.

Previous studies of polystyrene-toluene solutions by Bader and Cerf (*3*) and Dunbar et al. (*4*) have yielded conflicting results involving the sound velocity-concentration relationship. Bader (*3*) repots that sound velocity is independent of concentration from 0 to 13% whereas Dunbar (*4*) presents data showing a definite concentration dependence.

Table I. Molecular Weights of Polymer Samples

sample	M_w	M_n	M_v	M_w/M_n
PS A		9050	9 100	<1.06
PS B	263 000	68 300	290 000	3.85
PS C	1 790 000		1 840 000	<1.30

The effect of molecular weight on sound velocity in dilute polystyrene solutions was measured by Cochran et al. (*5*). He states that molecular weight has no effect on sound velocity but his values of sound velocity for 2.5% solutions of 4000 and 97 000 molecular weight polystyrene differ by as much as 4 m/s.

The purpose of this paper is to present data and to resolve the contradictions in the literature. To accomplish this objective, temperature and sound velocity were accurately measured. In addition, extreme care was taken to minimize contamination and concentration changes during measurement. The concentration dependency of the sound velocity was measured for polystyrene solutions between 0 and 19.75 wt %. The molecular weight dependency of the sound velocity was determined by using 1 and 10 wt % solutions of three different polystyrenes (9100, 290 000, and 1 840 000) in toluene.

Experimental Section

The polystyrene samples used in this study had the weight average (M_w), number average (M_n), and viscosity average (M_v) molecular weight values shown in Table I. Samples A and C

0021-9568/84/1729-0175$01.50/0 © 1984 American Chemical Society

were standard polystyrenes obtained from Pressure Chemical Co. and were used as received. Sample B was a commercial-grade polymer characterized by Dow Chemical Co. This sample was dried in a 50° air oven for 24 h and stored in a desiccator prior to use.

The toluene was Fisher Certified 99 mol % pure and used as received. Gas-chromatographic and infrared absorbance data supplied by Fisher indicated a purity of greater than 99.975 mol %. In addition, a sample of the toluene was examined by GC-MS indicating only trace quantities of benzene and xylene.

The monomer studied was Fisher Certified inhibited styrene having a purity of 99.6 mol %. The styrene was also used as received.

Sound velocity measurements were made with a MAPCO sonic solution monitor Model 6105. This instrument consists of an electronic processing circuit and a measurement probe. The sonic velocity measurement probe is comprised of a transmitting transducer, a receiving transducer, and a reflector mounted a fixed distance away providing a constant path length. The diameter of the path length was approximately 2.2 cm. The transducers are made of lead zirconate titanate. A sound pulse having a carrier frequency of 1.8 MHz is sent by the transmitting transducer, through the solution, and reflected back to the receiving transducer. The return signal triggers the transmitting transducer to send the next pulse. The pulse rate, dependent upon transit time and distance, and the time delay of the electronic circuit, thereby yields the velocity of sound of the solution. Calibration values supplied with the instrument for the sound path length and the electronic time delay were 0.08162 m and 3.15547×10^{-6} s, respectively.

Temperature measurements with an accuracy of 0.01 °C (traceable to NBS) and a precision of 0.001 °C were made by using a Hewlett-Packard digital quartz thermometer, Model 2801A. A one-point calibration of the thermometer using an ice bath as a reference was performed twice during the course of the investigation.

Density measurements with an accuracy of 0.0002 g/cm^3 (*6*) were made on the 0, 1, and 5 wt % solutions by using a Lipkin pycnometer and a Mettler analytical balance with a resolution of 0.0002 g. For solutions of higher polymer concentration, density measurements accurate to 0.0005 g/cm^3 were made with a bottle pycnometer.

Several precautions were taken to minimize solution contamination. First, all solution containers were glass, fitted with Teflon stoppers and stainless steel adapters. The solvent bottle was opened only once under nitrogen purge to install a dispenser. All subsequent transfers were made through stainless steel tubing with nitrogen pressure. Finally, the cell for the sound velocity probe, having a diameter of 5.2 cm and a height of 5.8 cm, was constructed entirely of stainless steel.

Results and Discussion

Sound velocity and density data were measured for pure toluene over the 10–50 °C range. The standard deviation of the sound velocity measurements at any given temperature varied between 0.10 and 0.21 m/s (standard deviations were based on a minimum of 10 values at each temperature). Two density determinations were performed at 10, 20, 30, 40, and 50 °C. The duplicate densities did not differ by more than 0.0001 g/cm^3.

Both Dunbar (*4*) and Freyer et al. (*7*) present sound velocity and density data for toluene. The density data determined by Dunbar and that determined in this study differ by less than 0.0003 g/cm^3 whereas the density data presented by Freyer is on the average 0.0010 g/cm^3 lower. The sound velocity data collected by Freyer and Dunbar are approximately 5 and 15 m/s higher than the sound velocity data collected in this investigation at any given temperature. The differences in these measurements could very well be caused by impurities in the toluene samples.

Table II. Least-Squares Coefficients for Pure Toluene

Polynomial Coefficients of Sound Velocity in m/s

$V = A + B(t) + C(t)^2$ with t in °C

polynomial degree	A	B	10^3C	max residual	no. of points
2	1414.7	−4.6313	3.5191	0.27	50

Polynomial Coefficients of Density in g/cm^3

$\rho = A + B(t) + C(t)^2$ with t in °C

polynomial degree	A	10^4B	10^6C	max residual	no. of points
2	0.884 06	−8.4286	−1.2857	0.000 02	10

Table III. Sound Velocity for Polystyrene[a] Solutions

[PS], wt %	sound velocity, m/s 10 °C	20 °C	30 °C	40 °C	50 °C
0.00	1368.8	1323.6	1279.2	1235.1	1192.0
1.01	1370.3	1325.1	1280.6	1237.0	1194.1
5.00	1375.6	1330.9	1286.7	1243.3	1200.8
9.06	1381.6	1337.1	1293.0	1249.9	1207.5
13.11	1389.6	1343.8	1300.1	1257.2	1215.0
19.75	1398.9	1356.0	1313.1	1271.1	1229.6

[a] Molecular weight = 290 000.

Table IV. Density of Polystyrene[a] Solutions

[PS], wt %	density, g/cm^3 10 °C	20 °C	30 °C	40 °C	50 °C
0.00	0.8755	0.8667	0.8576	0.8483	0.8387
1.01	0.8769	0.8681	0.8590	0.8489	0.8402
5.00	0.8843	0.8757	0.8667	0.8576	0.8481
9.06		0.8831	0.8733		
13.11		0.8906	0.8812		

[a] Molecular weight = 290 000.

Table V. Least-Squares Coefficients for Sound Velocity–Concentration Relationship of Polystyrene B in Toluene

Polynomial Coefficients of Sound Velocity in m/s

$V = A + B(x) + C(x)^2$ with x in wt %

temp, °C	$10^{-3}A$	B	10^3C	max residual	no. of points
10	1.368 64	1.460 94	4.3778	1.05	18
20	1.323 68	1.354 14	14.2248	0.10	18
30	1.279 24	1.367 99	17.4533	0.18	18
40	1.235 36	1.441 91	18.3867	0.27	18
50	1.192 36	1.506 08	18.8549	0.43	18

Polynomial regressions of the sound velocity and density of toluene as functions of temperature were examined. Although first-order regressions correlated both sound velocity and density with temperature accurately, second-order regressions lowered the maximum residuals to the uncertainty of the measurements. Table II presents the coefficients for the regressions of the sound velocity and density data of toluene between 10 and 50 °C.

The effect of polymer concentration on the sound velocity was studied by using the intermediate molecular weight polystyrene sample (sample B). Five concentrations between 0 and 20 wt % provided sufficient data to determine the sound velocity–concentration relationship for the dilute region. Tables III and IV present the sound velocity and density data for the intermediate molecular weight polystyrene solutions.

Figure 1 shows the sound velocity–concentration relationship for the polystyrene solutions at different temperatures. Slight upward curvature is observed at concentrations above 5 wt %.

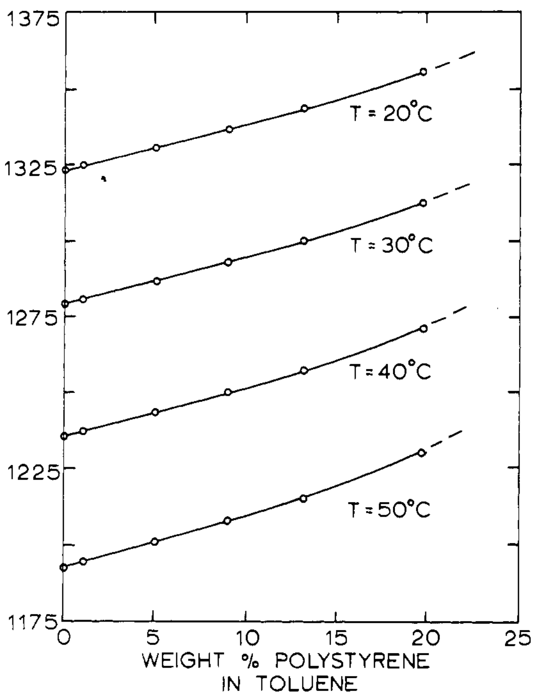

Figure 1. Sound velocity-concentration relationship for polystyrene B in toluene.

Table VI. Least-Squares Coefficients for Density-Concentration Relationship of Polystyrene B in Toluene

Polynomial Coefficients for Density in g/cm^3
$\rho = A + B(x)$ with x in wt % Polystyrene

temp, °C	A	10^3B	max residual	no. of points
20	0.866 49	1.8372	0.000 24	5
30	0.857 42	1.7984	0.000 42	5

Table VII. Adiabatic Compressibilities of Polystyrene B-Toluene Solutions

[PS B], wt %	adiabatic compressibility × 10^{10}, m^2/N				
	10 °C	20 °C	30 °C	40 °C	50 °C
0.00	6.096	6.586	7.126	7.728	8.392
1.01	6.073	6.560	7.099	7.698	8.347
5.00	5.976	6.447	6.969	7.543	8.177
9.06		6.334	6.849		
13.11		6.218	6.582		

This curvature tends to become more pronounced at the higher temperatures. The regression coefficients for these curves are presented in Table V.

Although the sound velocity-concentration relationship of the intermediate molecular weight solutions exhibited curvature, the density-concentration relationship was shown to be linear over the 0-13 wt % range. The regression coefficients for the density-concentration data collected at 20 and 30 °C are given in Table VI.

Adiabatic compressibility is readily calculated from sound velocity and density data and is equal to the reciprocal of the product of density and the square of the sound velocity. Table VII presents the adiabatic compressibilities for the intermediate molecular weight polystyrene solutions.

The effect of molecular weight on the sound velocity was studied by using 1 and 10 wt % solutions of the standard polystyrenes (Table I, A and C) in toluene. The sound velocities and densities of the standard and commercial polystyrene solutions given in Table VIII are invariant with molecular weight over the indicated concentration range. A slighly higher value of the sound velocity is observed for the 10 wt % solution of the 1 840 000 g/mol polystyrene as compared with the 10 wt % solutions of the other molecular weight polystyrenes at 30 °C. This difference in sound velocity could be caused by thermal gradients resulting from improper mixing of the highly viscous solution in the cell.

Table VIII. Sound Velocity and Density Data for Solutions of Various Molecular Weight Polystyrenes in Toluene

[PS], wt %	mol wt	sound velocity, m/s		
		20 °C	30 °C	40 °C
1.01	9 100	1325.3	1280.8	1236.8
1.01	290 000	1325.1	1280.6	1237.0
0.99	1 840 000	1325.3	1280.7	1236.8
10.25	9 100	1338.8	1294.8	1251.7
10.00	290 000	(1338.6	1294.7	1251.6)^a
10.06	1 840 000	1339.3	1295.8	1251.6

[PS], wt %	mol wt	density, g/cm^3	
		20 °C	30 °C
1.01	9 100	0.8684	0.8592
1.01	290 000	0.8681	0.8590
0.99	1 840 000	0.8686	0.8591
10.25	9 100	0.8850	0.8755
10.00	290 000	(0.8848	0.8754)^b
10.06	1 840 000	0.8846	0.8747

^{a} Interpolated for comparison by using a second-order regression equation for data in Table III. ^{b} Interpolated for comparison by using a linear regression of the data in Table IV.

Table IX. Sound Velocity Measurements for Solutions of Styrene Monomer in Toluene

[styrene], wt %	sound velocity, m/s		
	20 °C	30 °C	40 °C
0.00	1323.6	1279.2	1235.1
17.32	1335.4	1291.4	1248.1
51.15	1360.6	1316.9	1274.0
100.00	1397.9	1354.8	1312.5

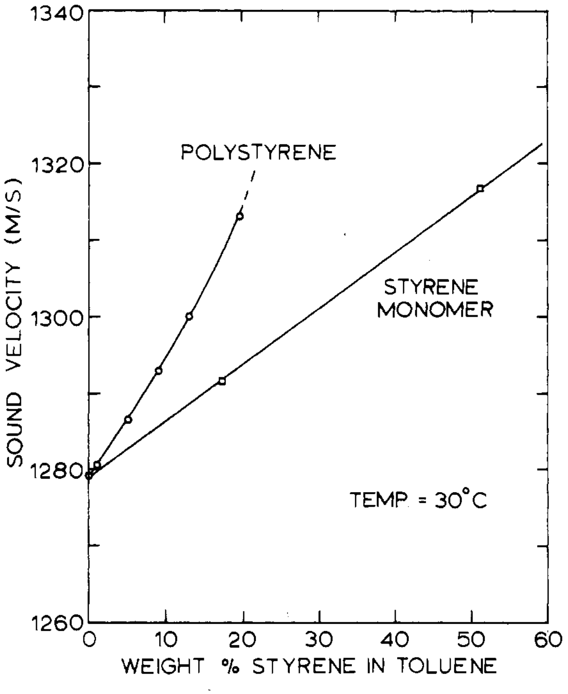

Figure 2. Comparison of styrene monomer and polymer sound velocity-concentration relationships.

To complete this study, ultrasonic measurements were made on styrene monomer and solutions of monomer in toluene. The sound velocity-concentration data shown in Table IX were found to be linear from 0 to 10 wt % styrene monomer in toluene.

The sound velocity-concentration relationships of the polymer and monomer in toluene, presented in Figure 2, are very different. The monomer curve has a smaller initial slope than the polymer curve and is linear. The polymer curve, however, exhibits slight upward curvature. The polymer curve represents polystyrenes having molecular weights between 9100 and 1 840 000. Between the monomer curve and polymer curve, a series of curves should exist which corresponds to molecular weights between 104, the molecular weight of the monomer, and 9100. The determination of these intermediate curves was beyond the scope of this study.

Conclusions

On the basis of the experimental measurements of this study, the following conclusions can be drawn:

(1) Sound velocity and density of 0-10 wt % solutions of polystyrene in toluene are independent of polymer molecular weight over the range from 9100 to 1 840 000.

(2) The sound velocity-concentration relationship for polystyrene in toluene from 0 to 20 wt % can be accurately described by using a second-order polynomial.

(3) The density-concentration relationship for polystyrene in toluene from 0 to 13 wt % is linear within experimental error.

(4) Toluene solutions of styrene monomer and polystyrenes having molecular weights greater than 9100 have measurably different sound velocity-concentration relationships. The polymer curve is concave and has a greater initial slope than the monomer curve which is a linear function of concentration.

Acknowledgment

We gratefully acknowledge T. C. Klingler and A. Platt of Dow Chemical for determining the number average and weight average molecular weight values for the polystyrene B sample.

Registry No. Polystyrene (homopolymer), 9003-53-6; styrene, 100-42-5.

Literature Cited

(1) Nozdrev, V. F. "Application of Ultrasonics in Molecular Physics"; Gordan and Breach: New York, 1963.
(2) Synder, S. J.; Synder, J. R. *J. Chem. Eng. Data* **1974**, *19*, 270.
(3) Bader, M.; Cerf, R. *Acustica* **1970**, *23*, 31.
(4) Dunbar, J. I.; North, A. M.; Pethrick, R. A.; Steinhauer, D. B. *J. Polymn. Sci., Polymn. Phys. Ed.* **1977**, *15*, 263.
(5) Cochran, M. A.; Dunbar, J. H.; North, A. M.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans 2* **1974**, *70*, 215.
(6) Lipkin, M. R.; Davison, J. A.; Harvey, W. T.; Kurtz, S. S. *Ind. Eng. Chem.* **1944**, *16*, 55.
(7) Freyer, E. B.; Hubbard, J. C.; Andrews, D. H. *J. Am. Chem. Soc.* **1929**, *51*, 759.

Received for review May 16, 1983. Accepted August 29, 1983.

Vapor-Liquid Equilibria of the Ternary System Methyl Borate-Methyl Alcohol-Benzene

Nicolai Münster, Charles A. Plank,* Walden L. S. Laukhuf, and Phoebus M. Christopher

Department of Chemical and Environmental Engineering, University of Louisville, Louisville, Kentucky 40292

Vapor-liquid equilibrium measurements at 101 325 Pa are reported for the methyl borate-methyl alcohol-benzene system. Analysis of the results shows that the ternary system can be reasonably represented from binary data by the Wilson equations and slightly better by the Margules correlations. The ternary system is made up of two minimum-boiling azeotropic systems and one ideal binary system. No ternary azeotrope exists.

The vapor-liquid equilbria have been measured for the ternary system methyl borate-methyl alcohol-benzene at 101 325 ± 133 Pa (760 ± 1 torr). An Altsheler (circulation type) still was used and is described in detail by Hala et al. (*1*). The present version, however, contains two thermocouples, one near the surface of the boiling liquid and one in the vapor space directly above the liquid level. These two thermocouples were both calibrated and in general gave the same values during operation. When they differed, the liquid thermocouple temperature was reported. Temperatures are believed to be accurate to ±0.1 K.

Materials Used

The methyl borate used was manufactured by the Aldrich Chemical Co., Inc., and was received at a nominal 99% purity. Methyl alcohol was manufactured by MCB Manufacturing Chemists, Inc., and received at a certified minimum purity of 99.8% with water content less than 0.1%, and a recorded boiling point of 337.75 K (64.6 °C). Benzene was manufactured by Burdick and Jackson Laboratories, Inc., and was specified with a purity greater than 99.5% and boiling point between 353.15 and 354.15 K (80-81 °C).

Chemicals were further purified by simple distillation. In the case of the methyl borate several distillations were performed to achieve a purity in excess of 99.9%. Approximately 50% of the original batch was recovered in this fashion. The standard mannitol-phenolphthalein method of analysis (*2*) for boric acid using 0.1 N sodium hydroxide was used for the analysis of the methyl borate. Properties of these compounds compared with literature values are shown in Table I.

Method of Analysis

Mixture analyses were made by a combination of chemical analysis and physical property measurements. This method has previously been used for systems of this type and found to be satisfactory (*6*). The same procedure was used here and involves the mannitol-sodium hydroxide titration for the methyl borate and measurement of the solution refractive index and solution density. Refractive indices were measured with a Bausch and Lomb Model 33-45-03 refractometer capable of precision to ±0.000 03 RI unit. The sodium D line (λ = 5893 Å) at 278.15 ± 0.05 K was used. Densities were determined by means of a pycnometer with a nominal value of 10 mL, at 278.15 ± 0.05 K. The pycnometer was calibrated with deionized water, specific resistance approximately 450 000, and weighed to ±0.0001 g. Analyses of known mixtures showed

0021-9568/84/1729-0178$01.50/0 © 1984 American Chemical Society