# Solubilities of 11 Polar Organic Solvents in Four Polymers Using the Piezoelectric−Quartz Sorption Method

**Gede Wibawa, Ryo Hatano, Yoshiyuki Sato, Shigeki Takishima, and Hirokatsu Masuoka***

Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

The solubilities of methanol, ethanol, propanol, 2-propanol, butanol, 2-butanol, 2-methyl-1-propanol, acetone, methyl ethyl ketone, methyl acetate, and propyl acetate in *cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate) were measured by the piezoelectric quartz crystal microbalance method at the four temperatures (293.2, 313.2, 333.2, and 353.2) K. In this work, four quartz crystals that were installed in an equilibrium cell enabled multiple solubility measurements. Estimated uncertainties of measured data were ±0.05 K for temperatures, ±0.9% for activities, and ±13.9% for mass fractions in the lowest solubility region, with a lower uncertainty being found in the higher solubility region. The activities obtained were correlated by the UNIQUAC equation with an overall AAD of 5.0%.

## Introduction

A knowledge of the solubilities of vapors of low-molecular-weight substances in polymers is needed for the design and operation of polymer plants so that residual monomers, oligomers, and polymerization solvents can be removed from polymer products as required to meet environment, health, and safety regulations. Vapor−liquid equilibria and solubility data have been measured for many years; yet, for systems containing polar solvents, the published data[1,2] are often only for infinite-dilution conditions. For wide range of concentrations, published solubility data[2,3] are limited in both the number of systems and the experimental conditions. For polyisoprene (PI), the available data are the values of Booth et al.[4] for solubility in acetone at 273.2 and 298.2 K. For poly(vinyl acetate) (PVAc), the available data are the values of Kokes et al.[5] for solubility in propanol and acetone at 303.2, 313.2, and 323.2 K.

In our previous paper,[6] the solubilities of seven nonpolar solvents (octane, cyclopentane, cyclohexane, benzene, toluene, ethylbenzene, and *p*-xylene) in *cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate) were reported, along with the reliability of the piezoelectric−quartz sorption method. This work is a part of our continued investigation into the applicability and reliability of a piezoelectric quartz crystal microbalance (QCM) apparatus for obtaining solvent solubilities in polymer solutions.[6−10] In the present study, emphasis is placed on the measurement of the solubilities of 11 polar solvents (methanol, ethanol, propanol, 2-propanol, butanol, 2-butanol, 2-methyl-1-propanol, acetone, methyl ethyl ketone, methyl acetate, and propyl acetate) in the same types of polymers [*cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate)] at (293.2, 313.2, 333.2, and 353.2) K.

## Experimental Section

**Materials.** All solvents were obtained from Katayama Chemicals with gas chromatography grade purities of 99.8 mass % for methanol; 99.5 mass % for ethanol and propanol; 99.7 mass % for 2-propanol; 99.0 mass % for butanol, 2-butanol, 2-methyl-1-propanol, acetone, methyl ethyl ketone, and propyl acetate; and 99.5 mass % for methyl acetate. All were used without further purification. The polymers were amorphous (Aldrich Chemical Co.), and their characteristics are shown in Table 1.

**Table 1. Characteristics[a] of Polymers**

| polymer | $T_g$ / K | $T_m$ / K | $10^{-3}\,M_w$ / g·mol$^{-1}$ |
|---|---|---|---|
| *cis*-1,4-polyisoprene | 202.2 | 309.2 | 800 |
| polyisobutylene | 197.2 | 274.7 | 500 |
| poly(*n*-butyl methacrylate) | 288.2 | − | 337 |
| poly(vinyl acetate) | 303.2 | − | 167 |

[a] $T_g$ = glass transition temperature, $T_m$ = melting temperature, $M_w$ = weight-average molar mass.

**Solubility Measurements.** Solubility measurements of 11 polar solvents (methanol, ethanol, propanol, 2-propanol, butanol, 2-butanol, 2-methyl-1-propanol, acetone, methyl ethyl ketone, methyl acetate and propyl acetate) in the polymers *cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate) at (293.2, 313.2, 333.2, and 353.2) K were made with a QCM apparatus. The four quartz-crystal sensors used in this work have specifications of 5 MHz, AT-cut, 5.5-mm diameter, and 0.3-mm thickness. They were installed in a sorption cell that enabled the simultaneous solubility measurements of a solvent vapor in four different polymers. The principle of the QCM method, experimental apparatus, procedure, and activity calculations from the measured variables were described fully in our previous paper.[6] For each solubility data point, the mass fraction of the solvent in the polymer, $w_1$, is obtained by the measurement of the frequency shift using the equation

$$w_1 = \frac{\Delta f_1}{\Delta f_0 + \Delta f_1} \tag{1}$$

where $\Delta f_0$ is the frequency shift due to the polymer coating on the crystal surface and $\Delta f_1$ is the additional frequency

* To whom correspondence should be addressed. Fax: +81-824-247721. E-mail: masuoka@hiroshima-u.ac.jp.

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**Table 2. Solubility of Methanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| PI | | PIB | | PBMA | | PVAc | | PI | | PIB | | PBMA | | PVAc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ |
| $T = 293.2$ K | | | | | | | | $T = 333.2$ K | | | | | | | |
| 0.272 | 0.002 | 0.272 | 0.002 | 0.268 | 0.006 | | | 0.103 | 0.004 | 0.190 | 0.006 | 0.190 | 0.010 | 0.190 | 0.021 |
| 0.495 | 0.005 | 0.495 | 0.004 | 0.609 | 0.036 | | | 0.200 | 0.006 | 0.374 | 0.009 | 0.374 | 0.023 | 0.374 | 0.047 |
| 0.681 | 0.009 | 0.681 | 0.006 | 0.747 | 0.063 | | | 0.378 | 0.010 | 0.580 | 0.013 | 0.425 | 0.027 | 0.425 | 0.056 |
| 0.864 | 0.015 | 0.864 | 0.009 | 0.834 | 0.092 | | | 0.476 | 0.012 | 0.749 | 0.018 | 0.580 | 0.043 | 0.580 | 0.088 |
| 0.965 | 0.024 | 0.965 | 0.014 | | | | | 0.592 | 0.014 | 0.851 | 0.022 | 0.661 | 0.055 | 0.661 | 0.109 |
| | | | | | | | | 0.678 | 0.016 | 0.896 | 0.028 | 0.749 | 0.072 | 0.749 | 0.137 |
| | | | | | | | | 0.771 | 0.019 | 0.950 | 0.039 | 0.851 | 0.102 | 0.851 | 0.193 |
| | | | | | | | | 0.849 | 0.022 | | | 0.896 | 0.126 | 0.896 | 0.245 |
| | | | | | | | | 0.906 | 0.027 | | | 0.950 | 0.171 | 0.950 | 0.341 |
| | | | | | | | | 0.943 | 0.033 | | | | | | |
| $T = 313.2$ K | | | | | | | | $T = 353.2$ K | | | | | | | |
| 0.103 | 0.002 | 0.103 | 0.001 | 0.194 | 0.009 | 0.194 | 0.018 | 0.092 | 0.002 | 0.092 | 0.002 | 0.092 | 0.004 | 0.092 | 0.007 |
| 0.193 | 0.003 | 0.193 | 0.002 | 0.366 | 0.019 | 0.366 | 0.038 | 0.181 | 0.005 | 0.181 | 0.004 | 0.181 | 0.011 | 0.181 | 0.016 |
| 0.282 | 0.004 | 0.282 | 0.003 | 0.555 | 0.033 | 0.555 | 0.069 | 0.283 | 0.008 | 0.283 | 0.006 | 0.283 | 0.019 | 0.283 | 0.028 |
| 0.365 | 0.005 | 0.365 | 0.004 | 0.637 | 0.042 | 0.637 | 0.090 | 0.377 | 0.010 | 0.377 | 0.008 | 0.377 | 0.027 | 0.377 | 0.040 |
| 0.454 | 0.007 | 0.454 | 0.005 | 0.675 | 0.048 | 0.675 | 0.102 | 0.457 | 0.013 | 0.457 | 0.010 | 0.457 | 0.035 | 0.457 | 0.053 |
| 0.543 | 0.009 | 0.543 | 0.007 | 0.739 | 0.058 | 0.739 | 0.122 | 0.558 | 0.016 | 0.558 | 0.012 | 0.558 | 0.048 | 0.558 | 0.073 |
| 0.612 | 0.010 | 0.612 | 0.008 | 0.782 | 0.067 | 0.782 | 0.140 | 0.622 | 0.019 | 0.622 | 0.015 | 0.622 | 0.061 | 0.578 | 0.079 |
| 0.704 | 0.012 | 0.704 | 0.011 | 0.820 | 0.077 | 0.820 | 0.157 | 0.721 | 0.024 | 0.721 | 0.018 | 0.721 | 0.087 | 0.656 | 0.100 |
| 0.777 | 0.015 | 0.777 | 0.014 | 0.867 | 0.094 | 0.867 | 0.185 | 0.800 | 0.030 | 0.800 | 0.021 | 0.800 | 0.108 | 0.750 | 0.133 |
| 0.850 | 0.019 | 0.850 | 0.021 | 0.920 | 0.118 | 0.920 | 0.229 | 0.897 | 0.041 | 0.897 | 0.025 | | | | |
| | | | | 0.937 | 0.131 | 0.937 | 0.255 | | | | | | | | |

**Table 3. Solubility of Ethanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| PI | | PIB | | PBMA | | PVAc | | PI | | PIB | | PBMA | | PVAc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ |
| $T = 293.2$ K | | | | | | | | $T = 333.2$ K | | | | | | | |
| 0.207 | 0.003 | 0.191 | 0.001 | 0.191 | 0.005 | | | 0.160 | 0.005 | 0.160 | 0.002 | 0.160 | 0.011 | 0.160 | 0.021 |
| 0.273 | 0.004 | 0.284 | 0.002 | 0.284 | 0.008 | | | 0.218 | 0.007 | 0.218 | 0.003 | 0.218 | 0.016 | 0.218 | 0.029 |
| 0.364 | 0.006 | 0.396 | 0.002 | 0.396 | 0.011 | | | 0.278 | 0.008 | 0.278 | 0.004 | 0.278 | 0.022 | 0.278 | 0.037 |
| 0.448 | 0.008 | 0.485 | 0.003 | 0.485 | 0.015 | | | 0.334 | 0.011 | 0.334 | 0.005 | 0.334 | 0.027 | 0.334 | 0.045 |
| 0.534 | 0.011 | 0.576 | 0.003 | 0.576 | 0.021 | | | 0.408 | 0.013 | 0.408 | 0.006 | 0.408 | 0.035 | 0.408 | 0.057 |
| 0.635 | 0.014 | 0.676 | 0.004 | 0.676 | 0.028 | | | 0.465 | 0.015 | 0.465 | 0.007 | 0.465 | 0.042 | 0.465 | 0.065 |
| 0.713 | 0.017 | 0.768 | 0.005 | 0.768 | 0.036 | | | 0.527 | 0.019 | 0.527 | 0.009 | 0.527 | 0.051 | 0.527 | 0.078 |
| 0.809 | 0.023 | 0.863 | 0.005 | 0.863 | 0.046 | | | 0.590 | 0.022 | 0.590 | 0.010 | 0.590 | 0.062 | 0.590 | 0.090 |
| 0.888 | 0.029 | 0.946 | 0.006 | 0.946 | 0.059 | | | 0.650 | 0.026 | 0.650 | 0.012 | 0.650 | 0.075 | 0.650 | 0.104 |
| | | | | | | | | 0.711 | 0.030 | 0.711 | 0.014 | 0.711 | 0.092 | 0.711 | 0.119 |
| | | | | | | | | 0.758 | 0.034 | 0.758 | 0.016 | 0.758 | 0.110 | 0.758 | 0.139 |
| | | | | | | | | 0.817 | 0.039 | 0.817 | 0.018 | 0.817 | 0.143 | 0.817 | 0.165 |
| | | | | | | | | 0.888 | 0.049 | 0.888 | 0.023 | 0.888 | 0.180 | | |
| | | | | | | | | 0.929 | 0.057 | 0.929 | 0.028 | | | | |
| $T = 313.2$ K | | | | | | | | $T = 353.2$ K | | | | | | | |
| 0.281 | 0.006 | 0.281 | 0.004 | 0.281 | 0.016 | 0.281 | 0.026 | 0.103 | 0.004 | 0.184 | 0.003 | 0.095 | 0.010 | 0.095 | 0.012 |
| 0.443 | 0.011 | 0.443 | 0.006 | 0.443 | 0.030 | 0.443 | 0.046 | 0.190 | 0.010 | 0.271 | 0.005 | 0.184 | 0.019 | 0.184 | 0.024 |
| 0.605 | 0.019 | 0.605 | 0.008 | 0.605 | 0.049 | 0.605 | 0.074 | 0.282 | 0.015 | 0.370 | 0.007 | 0.271 | 0.031 | 0.271 | 0.038 |
| 0.678 | 0.024 | 0.678 | 0.010 | 0.678 | 0.061 | 0.678 | 0.090 | 0.374 | 0.021 | 0.437 | 0.009 | 0.370 | 0.049 | 0.370 | 0.055 |
| 0.799 | 0.037 | 0.799 | 0.014 | 0.799 | 0.092 | 0.799 | 0.129 | 0.457 | 0.025 | | | 0.437 | 0.063 | 0.437 | 0.068 |
| 0.897 | 0.056 | 0.897 | 0.019 | 0.897 | 0.133 | 0.897 | 0.173 | 0.558 | 0.032 | | | | | | |
| 0.942 | 0.070 | 0.942 | 0.023 | 0.942 | 0.160 | 0.942 | 0.201 | 0.640 | 0.038 | | | | | | |
| | | | | | | | | 0.703 | 0.043 | | | | | | |
| | | | | | | | | 0.819 | 0.060 | | | | | | |
| | | | | | | | | 0.888 | 0.082 | | | | | | |

shift resulting from vapor sorption. The solvent activity was obtained by equating the fugacities of the solvent in the vapor and solution phases. The polymer can be considered nonvolatile, so by assuming the vapor phase to be pure solvent and estimating the pure-solvent fugacity through use of the second virial coefficient, the activity was obtained from

$$a_1 = \frac{P_1}{P_1^S}\exp\left[\frac{-B_1(P_1^S - P_1)}{RT}\right] \qquad (2)$$

where $P_1$ is the equilibrium pressure, which is equal to the vapor pressure of the solvent at the temperature of the solvent tank; $P_1^S$ is the vapor pressure of the solvent at the temperature of the sorption cell; and $R$ is the gas constant. The vapor pressures were calculated from the Wagner equation with constants given by Reid et al.[11] $B_1$ is the second virial coefficient of the solvent and was obtained from the correlation of Tsonopoulos.[12]

**Uncertainty Estimation.** Experimental uncertainty in this experiment might arise from the frequency and temperature measurements for both the solvent tank and the

**Table 4. Solubility of Propanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| PI | | PIB | | PBMA | | PVAc | | PI | | PIB | | PBMA | | PVAc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ |
| $T = 293.2$ K | | | | | | | | $T = 333.2$ K | | | | | | | |
| 0.289 | 0.005 | 0.289 | 0.003 | 0.289 | 0.020 | | | 0.156 | 0.010 | 0.156 | 0.006 | 0.156 | 0.017 | 0.156 | 0.024 |
| 0.390 | 0.007 | 0.390 | 0.004 | 0.390 | 0.029 | | | 0.261 | 0.015 | 0.261 | 0.008 | 0.261 | 0.029 | 0.261 | 0.038 |
| 0.480 | 0.009 | 0.480 | 0.006 | 0.480 | 0.040 | | | 0.390 | 0.021 | 0.390 | 0.012 | 0.390 | 0.046 | 0.390 | 0.057 |
| 0.577 | 0.011 | 0.577 | 0.007 | 0.577 | 0.053 | | | 0.496 | 0.027 | 0.496 | 0.015 | 0.496 | 0.065 | 0.496 | 0.075 |
| 0.669 | 0.013 | 0.669 | 0.008 | 0.669 | 0.070 | | | 0.615 | 0.034 | 0.615 | 0.019 | 0.615 | 0.091 | 0.615 | 0.099 |
| 0.758 | 0.016 | 0.758 | 0.010 | 0.758 | 0.091 | | | 0.714 | 0.042 | 0.714 | 0.024 | 0.714 | 0.127 | 0.714 | 0.125 |
| 0.856 | 0.021 | 0.856 | 0.014 | 0.856 | 0.126 | | | 0.837 | 0.055 | 0.837 | 0.032 | 0.837 | 0.190 | 0.837 | 0.175 |
| 0.948 | 0.027 | 0.948 | 0.019 | 0.948 | 0.176 | | | 0.937 | 0.073 | 0.937 | 0.046 | | | | |
| $T = 313.2$ K | | | | | | | | $T = 353.2$ K | | | | | | | |
| 0.103 | 0.002 | 0.200 | 0.006 | 0.200 | 0.017 | 0.200 | 0.020 | 0.107 | 0.008 | 0.107 | 0.003 | 0.107 | 0.014 | 0.107 | 0.014 |
| 0.193 | 0.004 | 0.370 | 0.010 | 0.370 | 0.033 | 0.370 | 0.040 | 0.289 | 0.019 | 0.191 | 0.008 | 0.191 | 0.031 | | 0.029 |
| 0.291 | 0.007 | 0.533 | 0.014 | 0.533 | 0.055 | 0.533 | 0.065 | 0.370 | 0.027 | 0.289 | 0.008 | 0.289 | 0.043 | 0.289 | 0.043 |
| 0.376 | 0.011 | 0.722 | 0.020 | 0.722 | 0.094 | 0.722 | 0.105 | 0.452 | 0.033 | 0.370 | 0.012 | 0.370 | 0.063 | 0.370 | 0.059 |
| 0.471 | 0.014 | 0.827 | 0.025 | 0.827 | 0.131 | 0.827 | 0.138 | 0.539 | 0.041 | 0.452 | 0.015 | 0.452 | 0.088 | 0.452 | 0.076 |
| 0.561 | 0.018 | 0.935 | 0.034 | 0.935 | 0.187 | 0.935 | 0.185 | 0.630 | 0.050 | 0.539 | 0.019 | 0.539 | 0.117 | 0.539 | 0.097 |
| 0.652 | 0.024 | | | | | | | 0.790 | 0.074 | 0.630 | 0.023 | | | 0.630 | 0.116 |
| 0.742 | 0.031 | | | | | | | 0.901 | 0.106 | 0.790 | 0.035 | | | | |
| 0.823 | 0.039 | | | | | | | | | 0.901 | 0.052 | | | | |
| 0.936 | 0.057 | | | | | | | | | | | | | | |

**Table 5. Solubility of 2-Propanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| PI | | PIB | | PBMA | | PVAc | | PI | | PIB | | PBMA | | PVAc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ |
| $T = 293.2$ K | | | | | | | | $T = 333.2$ K | | | | | | | |
| 0.184 | 0.004 | 0.184 | 0.001 | 0.184 | 0.011 | | | 0.102 | 0.003 | 0.102 | 0.002 | 0.102 | 0.009 | 0.102 | 0.011 |
| 0.275 | 0.005 | 0.275 | 0.002 | 0.275 | 0.017 | | | 0.191 | 0.007 | 0.191 | 0.004 | 0.191 | 0.018 | 0.191 | 0.022 |
| 0.362 | 0.007 | 0.362 | 0.003 | 0.362 | 0.024 | | | 0.289 | 0.011 | 0.289 | 0.006 | 0.289 | 0.029 | 0.289 | 0.036 |
| 0.451 | 0.009 | 0.451 | 0.004 | 0.451 | 0.032 | | | 0.381 | 0.016 | 0.381 | 0.008 | 0.381 | 0.040 | 0.381 | 0.050 |
| 0.538 | 0.012 | 0.538 | 0.005 | 0.538 | 0.042 | | | 0.470 | 0.021 | 0.470 | 0.011 | 0.470 | 0.055 | 0.470 | 0.066 |
| 0.645 | 0.017 | 0.645 | 0.007 | 0.645 | 0.058 | | | 0.562 | 0.028 | 0.562 | 0.013 | 0.562 | 0.073 | 0.562 | 0.086 |
| 0.700 | 0.020 | 0.700 | 0.008 | 0.700 | 0.069 | | | 0.649 | 0.036 | 0.649 | 0.017 | 0.649 | 0.097 | 0.649 | 0.110 |
| 0.793 | 0.027 | 0.793 | 0.011 | 0.793 | 0.095 | | | 0.730 | 0.046 | 0.730 | 0.022 | 0.730 | 0.126 | 0.730 | 0.136 |
| 0.872 | 0.036 | 0.872 | 0.016 | 0.872 | 0.128 | | | 0.818 | 0.062 | 0.818 | 0.028 | 0.818 | 0.170 | 0.818 | 0.172 |
| | | | | | | | | 0.907 | 0.087 | 0.907 | 0.039 | 0.907 | 0.237 | 0.907 | 0.225 |
| $T = 313.2$ K | | | | | | | | $T = 353.2$ K | | | | | | | |
| 0.101 | 0.002 | 0.101 | 0.001 | 0.101 | 0.006 | 0.101 | 0.006 | 0.104 | 0.005 | 0.104 | 0.002 | 0.104 | 0.010 | 0.104 | 0.012 |
| 0.187 | 0.004 | 0.187 | 0.002 | 0.187 | 0.013 | 0.187 | 0.013 | 0.193 | 0.011 | 0.193 | 0.005 | 0.193 | 0.022 | 0.193 | 0.024 |
| 0.283 | 0.007 | 0.283 | 0.003 | 0.283 | 0.022 | 0.283 | 0.024 | 0.283 | 0.017 | 0.283 | 0.008 | 0.283 | 0.034 | 0.283 | 0.039 |
| 0.371 | 0.009 | 0.371 | 0.005 | 0.371 | 0.031 | 0.371 | 0.036 | 0.371 | 0.025 | 0.371 | 0.011 | 0.371 | 0.049 | 0.371 | 0.054 |
| 0.463 | 0.013 | 0.463 | 0.006 | 0.463 | 0.042 | 0.463 | 0.051 | 0.462 | 0.033 | 0.462 | 0.015 | 0.462 | 0.066 | 0.462 | 0.073 |
| 0.546 | 0.016 | 0.546 | 0.008 | 0.546 | 0.055 | 0.546 | 0.062 | 0.555 | 0.043 | 0.555 | 0.019 | 0.555 | 0.088 | 0.555 | 0.095 |
| 0.642 | 0.022 | 0.642 | 0.010 | 0.642 | 0.075 | 0.642 | 0.082 | 0.640 | 0.054 | 0.640 | 0.024 | 0.640 | 0.112 | 0.640 | 0.118 |
| 0.734 | 0.030 | 0.734 | 0.014 | 0.734 | 0.102 | 0.734 | 0.106 | 0.769 | 0.078 | 0.769 | 0.034 | 0.769 | 0.166 | 0.769 | 0.163 |
| 0.823 | 0.041 | 0.823 | 0.020 | 0.823 | 0.142 | 0.823 | 0.138 | 0.856 | 0.106 | 0.856 | 0.045 | 0.856 | 0.227 | | |
| 0.906 | 0.057 | 0.906 | 0.026 | 0.906 | 0.208 | 0.906 | 0.184 | 0.942 | 0.148 | 0.942 | 0.064 | 0.942 | 0.339 | | |

**Table 6. Solubility of Butanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| | $w_1$ | | | | | $w_1$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | PI | PIB | PBMA | PVAc | $a_1$ | PI | PIB | PBMA | PVAc |
| $T = 293.2$ K | | | | | $T = 333.2$ K | | | | |
| 0.186 | 0.008 | 0.002 | 0.014 | – | 0.104 | 0.006 | 0.003 | 0.012 | 0.012 |
| 0.270 | 0.012 | 0.003 | 0.022 | – | 0.189 | 0.012 | 0.005 | 0.023 | 0.024 |
| 0.342 | 0.016 | 0.004 | 0.029 | – | 0.286 | 0.020 | 0.008 | 0.037 | 0.035 |
| 0.450 | 0.022 | 0.005 | 0.042 | – | 0.380 | 0.029 | 0.011 | 0.053 | 0.051 |
| 0.531 | 0.028 | 0.006 | 0.054 | – | 0.498 | 0.043 | 0.015 | 0.076 | 0.073 |
| 0.617 | 0.037 | 0.008 | 0.069 | – | 0.572 | 0.054 | 0.018 | 0.095 | 0.090 |
| 0.718 | 0.050 | 0.011 | 0.092 | – | 0.665 | 0.071 | 0.022 | 0.124 | 0.115 |
| 0.794 | 0.066 | 0.014 | 0.117 | – | 0.757 | 0.095 | 0.028 | 0.162 | 0.144 |
| 0.873 | 0.088 | 0.019 | 0.154 | – | 0.848 | 0.128 | 0.037 | 0.207 | 0.175 |
| | | | | | 0.934 | 0.174 | 0.048 | 0.268 | 0.223 |
| $T = 313.2$ K | | | | | $T = 353.2$ K | | | | |
| 0.103 | 0.005 | 0.002 | 0.010 | 0.007 | 0.103 | 0.009 | 0.004 | 0.015 | 0.012 |
| 0.192 | 0.011 | 0.004 | 0.019 | 0.015 | 0.201 | 0.021 | 0.010 | 0.032 | 0.029 |
| 0.277 | 0.016 | 0.006 | 0.030 | 0.026 | 0.299 | 0.033 | 0.014 | 0.050 | 0.047 |
| 0.365 | 0.023 | 0.008 | 0.041 | 0.038 | 0.396 | 0.046 | 0.019 | 0.070 | 0.066 |
| 0.451 | 0.031 | 0.010 | 0.055 | 0.051 | 0.508 | 0.062 | 0.024 | 0.096 | 0.092 |
| 0.552 | 0.042 | 0.012 | 0.074 | 0.070 | 0.589 | 0.076 | 0.028 | 0.119 | 0.112 |
| 0.635 | 0.053 | 0.015 | 0.095 | 0.087 | 0.679 | 0.095 | 0.033 | 0.149 | 0.138 |
| 0.716 | 0.069 | 0.019 | 0.122 | 0.107 | 0.766 | 0.117 | 0.041 | 0.186 | 0.171 |
| 0.798 | 0.090 | 0.024 | 0.159 | 0.132 | 0.854 | 0.146 | 0.054 | 0.245 | – |
| 0.898 | 0.139 | 0.036 | 0.232 | 0.233 | 0.948 | – | 0.074 | 0.355 | – |

**Table 7. Solubility of 2-Butanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| | $w_1$ | | | | | $w_1$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | PI | PIB | PBMA | PVAc | $a_1$ | PI | PIB | PBMA | PVAc |
| | $T = 293.2$ K | | | | | $T = 333.2$ K | | | |
| 0.178 | 0.005 | 0.002 | 0.017 | − | 0.097 | 0.006 | 0.004 | 0.013 | 0.013 |
| 0.262 | 0.008 | 0.004 | 0.025 | − | 0.184 | 0.012 | 0.007 | 0.026 | 0.025 |
| 0.336 | 0.010 | 0.005 | 0.033 | − | 0.280 | 0.019 | 0.011 | 0.043 | 0.041 |
| 0.419 | 0.013 | 0.006 | 0.049 | − | 0.358 | 0.025 | 0.014 | 0.056 | 0.055 |
| 0.493 | 0.017 | 0.008 | 0.055 | − | 0.448 | 0.033 | 0.018 | 0.076 | 0.073 |
| 0.577 | 0.021 | 0.010 | 0.071 | − | 0.535 | 0.042 | 0.023 | 0.100 | 0.094 |
| 0.656 | 0.027 | 0.014 | 0.089 | − | 0.611 | 0.052 | 0.028 | 0.125 | 0.116 |
| 0.750 | 0.036 | 0.019 | 0.119 | − | 0.698 | 0.067 | 0.036 | 0.160 | 0.143 |
| 0.830 | 0.048 | 0.026 | 0.153 | − | 0.787 | 0.087 | 0.047 | 0.204 | 0.178 |
| | | | | | 0.871 | 0.116 | 0.062 | 0.275 | − |
| | $T = 313.2$ K | | | | | $T = 353.2$ K | | | |
| 0.106 | 0.004 | 0.003 | 0.008 | 0.004 | 0.101 | 0.011 | 0.006 | 0.018 | 0.017 |
| 0.188 | 0.009 | 0.005 | 0.018 | 0.011 | 0.191 | 0.020 | 0.011 | 0.035 | 0.033 |
| 0.270 | 0.012 | 0.008 | 0.027 | 0.019 | 0.285 | 0.030 | 0.016 | 0.055 | 0.052 |
| 0.357 | 0.016 | 0.010 | 0.038 | 0.029 | 0.376 | 0.041 | 0.021 | 0.076 | 0.072 |
| 0.443 | 0.025 | 0.015 | − | − | 0.459 | 0.053 | 0.026 | 0.098 | 0.091 |
| 0.539 | 0.027 | 0.017 | 0.078 | 0.067 | 0.558 | 0.069 | 0.033 | 0.129 | 0.118 |
| 0.686 | 0.043 | 0.026 | 0.124 | 0.104 | 0.638 | 0.085 | 0.041 | 0.160 | − |
| 0.853 | 0.077 | 0.046 | 0.228 | 0.175 | 0.731 | 0.110 | 0.052 | 0.209 | − |
| | | | | | 0.812 | 0.139 | 0.067 | 0.253 | − |
| | | | | | 0.907 | 0.190 | 0.097 | 0.354 | 0.205 |

**Table 8. Solubility of 2-Methyl,1-Propanol in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| PI | | PIB | | PBMA | | PVAc | | PI | | PIB | | PBMA | | PVAc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ | $a_1$ | $w_1$ |
| $T = 293.2$ K | | | | | | | | $T = 333.2$ K | | | | | | | |
| 0.183 | 0.005 | 0.133 | 0.001 | 0.133 | 0.012 | | | 0.125 | 0.009 | 0.125 | 0.006 | 0.125 | 0.020 | 0.125 | 0.019 |
| 0.303 | 0.008 | 0.185 | 0.002 | 0.185 | 0.017 | | | 0.282 | 0.018 | 0.282 | 0.010 | 0.282 | 0.040 | 0.282 | 0.041 |
| 0.444 | 0.013 | 0.262 | 0.003 | 0.262 | 0.025 | | | 0.416 | 0.025 | 0.416 | 0.014 | 0.416 | 0.062 | 0.416 | 0.063 |
| 0.595 | 0.018 | 0.355 | 0.004 | 0.355 | 0.035 | | | 0.571 | 0.037 | 0.571 | 0.020 | 0.571 | 0.098 | 0.571 | 0.096 |
| 0.827 | 0.033 | 0.450 | 0.005 | 0.450 | 0.047 | | | 0.727 | 0.058 | 0.727 | 0.030 | 0.727 | 0.153 | 0.727 | 0.145 |
| 0.906 | 0.040 | 0.543 | 0.007 | 0.543 | 0.061 | | | 0.882 | 0.095 | 0.882 | 0.048 | 0.882 | 0.249 | 0.882 | 0.227 |
| 0.969 | 0.044 | 0.633 | 0.009 | 0.633 | 0.079 | | | 0.935 | 0.110 | 0.935 | 0.055 | 0.935 | 0.281 | 0.935 | 0.243 |
| | | 0.722 | 0.011 | 0.722 | 0.098 | | | | | | | | | | |
| | | 0.792 | 0.014 | 0.792 | 0.120 | | | | | | | | | | |
| | | 0.866 | 0.018 | 0.866 | 0.146 | | | | | | | | | | |
| $T = 313.2$ K | | | | | | | | $T = 353.2$ K | | | | | | | |
| 0.108 | 0.005 | 0.108 | 0.003 | 0.108 | 0.012 | 0.108 | 0.006 | 0.109 | 0.012 | 0.106 | 0.005 | 0.106 | 0.017 | 0.106 | 0.017 |
| 0.236 | 0.010 | 0.236 | 0.007 | 0.236 | 0.028 | 0.236 | 0.020 | 0.248 | 0.024 | 0.202 | 0.010 | 0.202 | 0.034 | 0.202 | 0.035 |
| 0.393 | 0.017 | 0.393 | 0.011 | 0.393 | 0.050 | 0.393 | 0.044 | 0.383 | 0.035 | 0.298 | 0.014 | 0.298 | 0.053 | 0.298 | 0.054 |
| 0.527 | 0.023 | 0.527 | 0.015 | 0.527 | 0.075 | 0.527 | 0.071 | 0.511 | 0.048 | 0.387 | 0.018 | 0.387 | 0.073 | 0.387 | 0.073 |
| 0.644 | 0.032 | 0.644 | 0.020 | 0.644 | 0.106 | 0.644 | 0.097 | 0.659 | 0.070 | 0.488 | 0.023 | 0.488 | 0.100 | 0.488 | 0.099 |
| 0.767 | 0.045 | 0.767 | 0.027 | 0.767 | 0.151 | 0.767 | 0.131 | 0.766 | 0.092 | 0.580 | 0.028 | 0.580 | 0.129 | 0.580 | 0.126 |
| 0.832 | 0.055 | 0.832 | 0.032 | 0.832 | 0.179 | 0.832 | 0.154 | 0.856 | 0.126 | 0.668 | 0.035 | 0.668 | 0.162 | 0.668 | 0.156 |
| 0.940 | 0.076 | 0.940 | 0.044 | 0.940 | 0.244 | 0.940 | 0.202 | 0.930 | 0.165 | 0.767 | 0.044 | 0.767 | 0.209 | 0.767 | 0.194 |
| | | | | | | | | | | 0.862 | 0.061 | 0.862 | 0.284 | | |
| | | | | | | | | | | 0.930 | 0.077 | | | | |

sorption cell. The solvent tank and the sorption cell temperatures were measured with an accuracy of ±0.03 K and were controlled to within ±0.02 K at the desired temperatures. The uncertainty in temperature, including its control, was within ±0.05 K. Fluctuations in the frequency at equilibrium were ±5 Hz throughout this study. An uncertainty analysis shows that the maximum uncertainty in the mass fraction of solvent was ±13.9%, which was observed in the lowest solubility region. In the higher solubility region, the uncertainty was lower. Considering the uncertainty in the temperature measurements, the vapor pressure correlation, and the Tsonopolous correlation[12] for the second virial coefficients, the uncertainty in solvent activity was estimated to be less than ±0.9%.

## Results and Discussion

Because all measurements were made above the polymer glass transition temperatures, data were not measured for systems containing poly(vinyl acetate) at the temperature of 293.2 K. Experimental solubility data for 44 solvent + polymer systems at temperatures of (293.2, 313.2, 333.2, and 353.2) K are shown in Tables 2−12. The reliability of the measurements was confirmed by comparing the present data with existing published data for the systems of acetone

**Table 9. Solubility of Acetone in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| | $w_1$ | | | | | $w_1$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | PI | PIB | PBMA | PVAc | $a_1$ | PI | PIB | PBMA | PVAc |
| | | $T$ = 293.2 K | | | | | $T$ = 333.2 K | | |
| 0.302 | 0.012 | 0.007 | 0.032 | – | 0.099 | 0.011 | 0.006 | 0.015 | 0.017 |
| 0.395 | 0.018 | 0.011 | 0.048 | – | 0.192 | 0.020 | 0.010 | 0.030 | 0.035 |
| 0.490 | 0.024 | 0.014 | 0.067 | – | 0.275 | 0.030 | 0.015 | 0.045 | 0.054 |
| 0.579 | 0.031 | 0.018 | 0.088 | – | 0.377 | 0.042 | 0.021 | 0.069 | 0.081 |
| 0.670 | 0.041 | 0.022 | 0.117 | – | 0.452 | 0.053 | 0.025 | 0.090 | 0.104 |
| 0.773 | 0.053 | 0.028 | 0.159 | – | 0.539 | 0.068 | 0.032 | 0.124 | 0.138 |
| 0.865 | 0.070 | 0.034 | 0.237 | – | 0.633 | 0.087 | 0.039 | 0.170 | 0.175 |
| 0.942 | 0.088 | 0.041 | – | – | 0.720 | 0.107 | 0.048 | – | – |
| | | | | | 0.816 | 0.138 | 0.061 | – | – |
| | | | | | 0.890 | 0.169 | 0.071 | – | – |
| | | | | | 0.932 | 0.192 | 0.078 | – | – |
| | | $T$ = 313.2 K | | | | | $T$ = 353.2 K | | |
| 0.133 | 0.011 | 0.004 | 0.014 | 0.025 | 0.098 | 0.010 | 0.004 | 0.015 | 0.019 |
| 0.193 | 0.016 | 0.007 | 0.023 | 0.037 | 0.181 | 0.019 | 0.009 | 0.030 | 0.037 |
| 0.285 | 0.024 | 0.010 | 0.037 | 0.057 | 0.267 | 0.029 | 0.014 | 0.049 | 0.058 |
| 0.394 | 0.034 | 0.016 | 0.055 | 0.082 | 0.359 | 0.041 | 0.021 | 0.075 | 0.081 |
| 0.473 | 0.043 | 0.022 | 0.073 | 0.104 | 0.448 | 0.055 | 0.029 | 0.108 | 0.106 |
| 0.577 | 0.055 | 0.027 | 0.099 | 0.136 | 0.540 | 0.070 | 0.038 | 0.135 | – |
| 0.667 | 0.068 | 0.034 | 0.132 | 0.167 | 0.631 | 0.088 | 0.049 | – | – |
| 0.768 | 0.088 | 0.044 | 0.195 | 0.223 | 0.727 | 0.111 | 0.061 | – | – |
| 0.882 | 0.118 | 0.059 | – | – | 0.821 | 0.140 | 0.075 | – | – |
| 0.941 | 0.139 | 0.067 | – | – | 0.913 | 0.184 | 0.090 | – | – |

**Table 10. Solubility of Methyl Ethyl Ketone in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| | $w_1$ | | | | | $w_1$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | PI | PIB | PBMA | PVAc | $a_1$ | PI | PIB | PBMA | PVAc |
| | | $T$ = 293.2 K | | | | | $T$ = 333.2 K | | |
| 0.271 | 0.016 | 0.010 | 0.036 | – | 0.109 | 0.013 | 0.008 | 0.020 | 0.022 |
| 0.409 | 0.033 | 0.019 | 0.074 | – | 0.352 | 0.051 | 0.030 | 0.076 | 0.085 |
| 0.476 | 0.042 | 0.024 | 0.095 | – | 0.601 | 0.111 | 0.062 | 0.161 | 0.169 |
| 0.566 | 0.055 | 0.031 | 0.122 | – | 0.891 | 0.231 | 0.125 | 0.353 | – |
| 0.662 | 0.074 | 0.039 | 0.162 | – | | | | | |
| 0.753 | 0.097 | 0.048 | 0.209 | – | | | | | |
| 0.837 | 0.132 | 0.062 | 0.280 | – | | | | | |
| 0.953 | 0.195 | 0.083 | – | – | | | | | |
| | | $T$ = 313.2 K | | | | | $T$ = 353.2 K | | |
| 0.195 | 0.021 | 0.014 | 0.036 | 0.039 | 0.098 | 0.012 | 0.006 | 0.015 | 0.015 |
| 0.450 | 0.059 | 0.033 | 0.101 | 0.111 | 0.184 | 0.027 | 0.014 | 0.037 | 0.039 |
| 0.615 | 0.101 | 0.052 | 0.159 | 0.173 | 0.264 | 0.041 | 0.022 | 0.057 | 0.059 |
| 0.720 | 0.143 | 0.069 | 0.213 | 0.223 | 0.349 | 0.057 | 0.033 | 0.081 | 0.082 |
| 0.815 | – | 0.088 | 0.281 | 0.287 | 0.454 | 0.080 | 0.047 | 0.124 | 0.113 |
| | | | | | 0.546 | 0.102 | 0.061 | 0.163 | 0.147 |
| | | | | | 0.632 | 0.127 | 0.076 | – | 0.163 |
| | | | | | 0.715 | 0.156 | 0.090 | – | – |
| | | | | | 0.795 | 0.192 | 0.101 | – | – |
| | | | | | 0.888 | 0.238 | – | – | – |

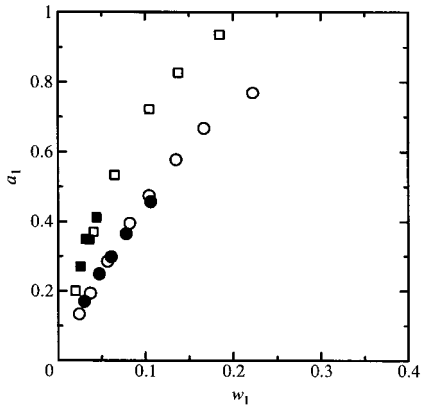


**Figure 1.** Comparisons between present work and published data at 313.2 K. Activity of solvent $a_1$ versus solvent mass fraction $w_1$ for propanol (1) + poly(vinyl acetate) (2) (□, this work; ■, Kokes et al.)[5] and for acetone (1) + poly(vinyl acetate) (2) (○, this work; ●, Kokes et al.[5]).

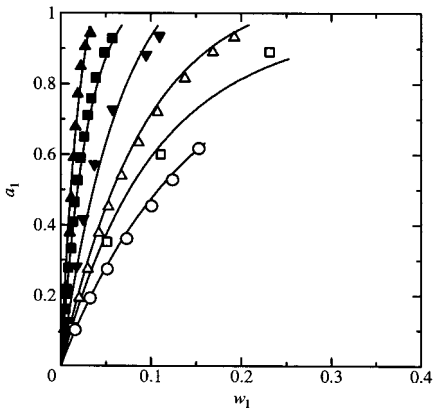


**Figure 2.** Activity of solvent $a_1$ vs solvent mass fraction $w_1$ in solvent + *cis*-1,4-polyisoprene systems at 333.2 K: ▲, methanol (1) + *cis*-1,4-polyisoprene (2); ■, ethanol (1) + *cis*-1,4-polyisoprene (2); ▼, 2-methyl-1-propanol (1) + *cis*-1,4-polyisoprene (2); △, acetone (1) + *cis*-1,4-polyisoprene (2); □, methyl ethyl ketone (1) + *cis*-1,4-polyisoprene (2); ○, propyl acetate (1) + *cis*-1,4-polyisoprene (2); lines, calculated with the UNIQUAC equation.

**Table 11. Solubility of Methyl Acetate in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| | $w_1$ | | | | | $w_1$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | PI | PIB | PBMA | PVAc | $a_1$ | PI | PIB | PBMA | PVAc |
| | | $T = 293.2$ K | | | | | $T = 333.2$ K | | |
| 0.276 | 0.019 | 0.016 | 0.047 | – | 0.103 | 0.013 | 0.007 | 0.018 | 0.025 |
| 0.361 | 0.027 | 0.022 | 0.065 | – | 0.189 | 0.024 | 0.014 | 0.034 | 0.048 |
| 0.464 | 0.040 | 0.030 | 0.090 | – | 0.273 | 0.038 | 0.021 | 0.052 | 0.073 |
| 0.544 | 0.052 | 0.037 | 0.114 | – | 0.361 | 0.054 | 0.029 | 0.074 | 0.101 |
| 0.631 | 0.071 | 0.045 | 0.147 | – | 0.447 | 0.074 | 0.037 | 0.098 | 0.131 |
| 0.718 | 0.094 | 0.055 | 0.185 | – | 0.531 | 0.095 | 0.046 | 0.125 | 0.161 |
| 0.805 | 0.131 | 0.067 | 0.242 | – | 0.626 | 0.123 | 0.059 | 0.164 | 0.201 |
| 0.906 | 0.190 | 0.084 | 0.325 | – | 0.719 | 0.151 | 0.074 | 0.210 | – |
| | | | | | 0.796 | 0.172 | 0.091 | 0.259 | – |
| | | | | | 0.879 | – | 0.113 | 0.348 | – |
| | | $T = 313.2$ K | | | | | $T = 353.2$ K | | |
| 0.192 | 0.021 | 0.013 | 0.034 | 0.048 | 0.102 | 0.013 | 0.007 | 0.018 | 0.024 |
| 0.267 | 0.030 | 0.018 | 0.049 | 0.070 | 0.190 | 0.028 | 0.014 | 0.036 | 0.047 |
| 0.359 | 0.045 | 0.025 | 0.070 | 0.100 | 0.275 | 0.044 | 0.023 | 0.056 | 0.072 |
| 0.439 | 0.060 | 0.032 | 0.090 | 0.129 | 0.365 | 0.061 | 0.032 | 0.079 | 0.098 |
| 0.528 | 0.080 | 0.041 | 0.118 | 0.164 | 0.458 | 0.082 | 0.044 | 0.107 | 0.128 |
| 0.607 | 0.101 | 0.050 | 0.146 | 0.198 | 0.549 | 0.100 | 0.058 | 0.138 | 0.158 |
| 0.710 | 0.138 | 0.063 | 0.196 | 0.251 | 0.634 | – | 0.072 | 0.172 | – |
| 0.777 | 0.168 | 0.074 | 0.237 | – | 0.723 | – | 0.088 | 0.216 | – |
| 0.864 | 0.208 | 0.091 | 0.308 | – | 0.810 | – | 0.106 | 0.287 | – |
| | | | | | 0.890 | – | 0.122 | 0.351 | – |

**Table 12. Solubility of Propyl Acetate in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc) Represented in Terms of Solvent Activity, $a_1$, and Mass Fraction, $w_1$**

| | $w_1$ | | | | | $w_1$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a_1$ | PI | PIB | PBMA | PVAc | $a_1$ | PI | PIB | PBMA | PVAc |
| | | $T = 293.2$ K | | | | | $T = 333.2$ K | | |
| 0.265 | 0.036 | 0.025 | 0.057 | – | 0.101 | 0.016 | 0.011 | 0.022 | 0.021 |
| 0.361 | 0.053 | 0.036 | 0.083 | – | 0.191 | 0.033 | 0.021 | 0.044 | 0.041 |
| 0.432 | 0.068 | 0.045 | 0.106 | – | 0.275 | 0.052 | 0.031 | 0.067 | 0.062 |
| 0.517 | 0.088 | 0.056 | 0.135 | – | 0.359 | 0.073 | 0.043 | 0.092 | 0.087 |
| 0.606 | 0.116 | 0.072 | 0.174 | – | 0.454 | 0.102 | 0.058 | 0.126 | 0.117 |
| 0.684 | 0.147 | 0.086 | 0.214 | – | 0.528 | 0.125 | 0.070 | 0.155 | 0.144 |
| 0.762 | 0.188 | 0.105 | 0.263 | – | 0.616 | 0.154 | 0.089 | 0.194 | 0.179 |
| 0.852 | 0.233 | 0.131 | 0.320 | – | 0.704 | – | 0.113 | 0.239 | 0.222 |
| | | | | | 0.793 | – | 0.144 | 0.304 | – |
| | | | | | 0.879 | – | 0.176 | 0.398 | – |
| | | $T = 313.2$ K | | | | | $T = 353.2$ K | | |
| 0.100 | 0.012 | 0.009 | 0.020 | 0.012 | 0.101 | 0.018 | 0.011 | 0.023 | 0.021 |
| 0.190 | 0.026 | 0.018 | 0.040 | 0.033 | 0.194 | 0.039 | 0.023 | 0.047 | 0.044 |
| 0.277 | 0.041 | 0.028 | 0.061 | 0.055 | 0.289 | 0.062 | 0.035 | 0.074 | 0.069 |
| 0.369 | 0.060 | 0.040 | 0.087 | 0.081 | 0.369 | 0.082 | 0.049 | 0.100 | 0.091 |
| 0.456 | 0.083 | 0.052 | 0.115 | 0.108 | 0.459 | 0.105 | 0.065 | 0.132 | 0.118 |
| 0.532 | 0.106 | 0.064 | 0.143 | 0.135 | 0.552 | 0.127 | 0.085 | 0.166 | 0.150 |
| 0.618 | 0.139 | 0.080 | 0.181 | 0.172 | 0.641 | – | 0.105 | 0.206 | 0.181 |
| 0.701 | 0.173 | 0.097 | 0.224 | 0.208 | 0.728 | – | 0.125 | 0.255 | – |
| 0.793 | 0.208 | 0.120 | 0.277 | 0.261 | 0.809 | – | 0.142 | 0.301 | – |
| 0.878 | – | 0.151 | 0.356 | – | 0.898 | – | 0.167 | 0.374 | – |

+ poly(vinyl acetate) and propanol + poly(vinyl acetate)[5] at 313.2 K. Our data agreed well with the published data, as presented in Figure 1. Published data for the acetone + polyisoprene system[4] at 298.2 K agreed reasonably well, with an average absolute deviation (AAD) of 7.8% compared to results calculated from one set of the UNIQUAC parameters obtained in this work (Table 13) that will be described in detail later.

To examine whether any trends related to structural effects of the solvents could be observed, the solubilities of three solvents (methanol, ethanol, and 2-methyl-1-propanol) representing polar solvents with hydrogen bonding and three solvents (acetone, methyl ethyl ketone, and propyl acetate) representing polar solvents without hydrogen bonding in *cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate) at 333.2 K were plotted, as presented in Figures 2−5, respectively. These figures show that the solubilities of the solvents are strongly influenced by their polarities. The solubilities of polar solvents with hydrogen bonding are lower than those of polar solvents without hydrogen bonding in the four polymers in this study. For alcoholic solvents, the effect of solvent compounds on solubility is not significant in both polyisobutylene and poly(vinyl acetate), as shown in Figures 3 and 5, respectively. For polar solvents without hydrogen bonding, the effect of solvent compounds on solubility is not significant in both poly(*n*-butyl methacrylate) and poly(vinyl acetate), as shown in Figures 4 and 5, respectively. Among all of the solvents studied, propyl acetate is most soluble in *cis*-1,4-polyisoprene, polyisobu-

**Table 13. Temperature-Independent Parameters of the UNIQUAC Equation (eq 3) and Average Absolute Deviations (AADs) between Measured and Calculated Solvent Activities**

| polymer[a] | solvent | $a_{12}^{(0)}$ | $a_{12}^{(1)}$ | $a_{21}^{(0)}$ | $a_{21}^{(1)}$ | AAD[b] |
|---|---|---|---|---|---|---|
| | | K | | K | | % |
| PI[c] | methanol | −140.81 | 2.13 | 960.31 | −4.16 | 10.6 |
| | ethanol | −234.32 | 1.82 | 707.02 | −4.56 | 4.6 |
| | propanol | −165.48 | 0.79 | 521.39 | −2.79 | 7.8 |
| | 2-propanol | −246.58 | 1.66 | 675.99 | −4.43 | 3.8 |
| | butanol | −170.71 | 1.07 | 408.01 | −2.44 | 3.4 |
| | 2-butanol | −184.65 | 1.67 | 465.61 | −3.77 | 3.2 |
| | 2-methyl-1-propanol | −128.07 | 1.58 | 372.16 | −3.16 | 6.3 |
| | acetone | −17.40 | −0.01 | 296.20 | −1.18 | 8.3 |
| | MEK | −103.99 | 0.24 | 316.98 | −1.15 | 5.2 |
| | methyl acetate | −105.54 | −0.25 | 357.46 | −0.63 | 4.8 |
| | propyl acetate | −124.78 | 0.55 | 269.54 | −1.22 | 2.8 |
| PIB[c] | methanol | −122.89 | 0.40 | 1007.30 | −1.80 | 9.6 |
| | ethanol | −211.79 | −0.41 | 797.39 | −0.82 | 8.2 |
| | propanol | −101.70 | −0.09 | 429.88 | −0.80 | 14.5 |
| | 2-propanol | −264.90 | 0.80 | 814.94 | −3.36 | 4.4 |
| | butanol | −189.63 | 0.62 | 555.01 | −2.32 | 8.2 |
| | 2-butanol | −203.41 | 0.72 | 563.49 | −2.60 | 7.9 |
| | 2-methyl-1-propanol | −129.37 | 0.09 | 440.02 | −1.41 | 14.2 |
| | acetone | −98.67 | 0.09 | 479.28 | −0.90 | 5.6 |
| | MEK | −88.53 | −0.35 | 339.92 | 0.00 | 6.1 |
| | methyl acetate | −63.95 | 0.08 | 319.43 | −0.17 | 1.5 |
| | propyl acetate | −76.65 | 0.42 | 220.12 | −0.53 | 1.5 |
| PBMA[c] | methanol | −112.98 | 0.88 | 654.49 | −2.39 | 4.2 |
| | ethanol | −128.48 | 0.13 | 456.27 | −2.59 | 3.5 |
| | propanol | −140.51 | 2.46 | 317.73 | −3.90 | 2.6 |
| | 2-propanol | −129.51 | 0.54 | 325.72 | −1.64 | 1.6 |
| | butanol | −89.33 | 0.98 | 217.45 | −1.87 | 1.7 |
| | 2-butanol | −107.67 | 1.07 | 237.49 | −2.11 | 3.7 |
| | 2-methyl-1-propanol | 17.57 | 0.71 | 82.07 | −1.29 | 2.1 |
| | acetone | −64.74 | −1.08 | 249.95 | 0.69 | 3.0 |
| | MEK | −64.36 | −0.73 | 168.35 | 0.64 | 3.6 |
| | methyl acetate | −19.11 | −0.18 | 124.50 | 0.19 | 0.7 |
| | propyl acetate | 4.07 | 1.16 | 43.81 | −1.03 | 1.7 |
| PVAc[d] | methanol | 62.50 | −1.27 | 123.58 | 2.50 | 3.6 |
| | ethanol | 31.96 | 1.25 | 99.08 | −1.93 | 3.6 |
| | propanol | 127.60 | 1.39 | −2.27 | −1.55 | 3.8 |
| | 2-propanol | −97.49 | 0.31 | 267.38 | −1.54 | 5.3 |
| | butanol | −95.95 | 0.91 | 230.21 | −1.94 | 4.3 |
| | 2-butanol | −88.75 | 0.86 | 222.85 | −2.01 | 10.9 |
| | 2-methyl-1-propanol | −77.25 | 0.84 | 217.97 | −2.19 | 6.5 |
| | acetone | 255.58 | −3.36 | −148.73 | 2.84 | 1.9 |
| | MEK | 145.46 | 1.54 | −84.62 | −0.75 | 3.4 |
| | methyl acetate | 185.03 | 1.37 | −109.03 | −0.58 | 0.9 |
| | propyl acetate | 38.05 | 0.54 | 11.35 | −0.53 | 3.6 |
| overall | | | | | | 5.0 |

[a] PI = *cis*-1,4-polyisoprene, PIB = polyisobutylene, PBMA = poly(*n*-butyl methacrylate), PVAc = poly(vinyl acetate). [b] AAD = $(1/N)|a_1^{\text{calcd}} - a_1^{\text{expt}}|/a_1^{\text{expt}} \times 100$, where $N$ = number of data points and superscripts calcd and expt denote the calculated and experimental values, respectively. [c] Temperature range = 293.2−353.2 K. [d] Temperature range = 313.2−353.2 K.

tylene, and poly(*n*-butyl methacrylate). The polar solvents were found to be more soluble in polar polymers [poly(*n*-butyl methacrylate) and poly(vinyl acetate)] than in nonpolar polymers [*cis*-1,4-polyisoprene and polyisobutylene], as shown in Figure 6. All polar solvents studied exhibited the lowest solubilities in polyisobutylene.

The solvent activities were correlated with the UNIQUAC equation[13] with interaction parameters defined by a linear function of temperature

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)}(T/\text{K} - 273.15) \qquad (3)$$

where $a_{12}^{(0)}$, $a_{12}^{(1)}$, $a_{21}^{(0)}$, and $a_{21}^{(1)}$ are temperature-independent

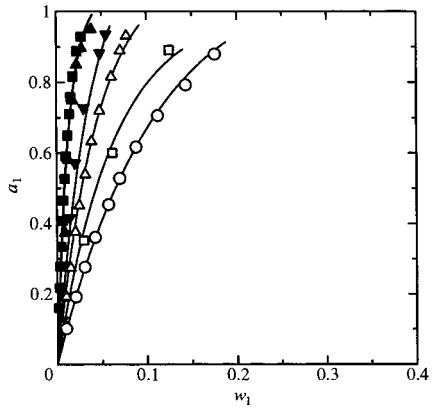


**Figure 3.** Activity of solvent $a_1$ vs solvent mass fraction $w_1$ in solvent + polyisobutylene systems at 333.2 K: ▲, methanol (1) + polyisobutylene (2); ■, ethanol (1) + polyisobutylene (2); ▼, 2-methyl-1-propanol (1) + polyisobutylene (2); △, acetone (1) + polyisobutylene (2); □, methyl ethyl ketone (1) + polyisobutylene (2); ○, propyl acetate (1) + polyisobutylene (2); lines, calculated with the UNIQUAC equation.

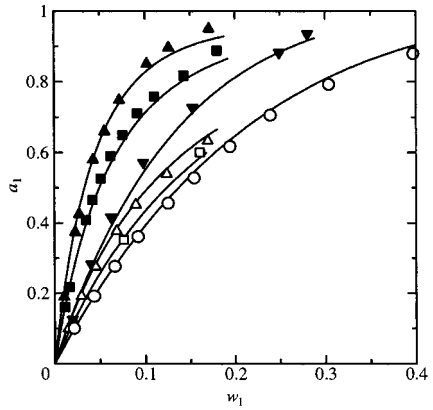


**Figure 4.** Activity of solvent $a_1$ vs solvent mass fraction $w_1$ in solvent + poly(*n*-butyl methacrylate) systems at 333.2 K: ▲, methanol (1) + poly(*n*-butyl methacrylate) (2); ■, ethanol (1) + poly(*n*-butyl methacrylate) (2); ▼, 2-methyl-1-propanol (1) + poly(*n*-butyl methacrylate) (2); △, acetone (1) + poly(*n*-butyl methacrylate) (2); □, methyl ethyl ketone (1) + poly(*n*-butyl methacrylate) (2); ○, propyl acetate (1) + poly(*n*-butyl methacrylate) (2); lines, calculated with the UNIQUAC equation.

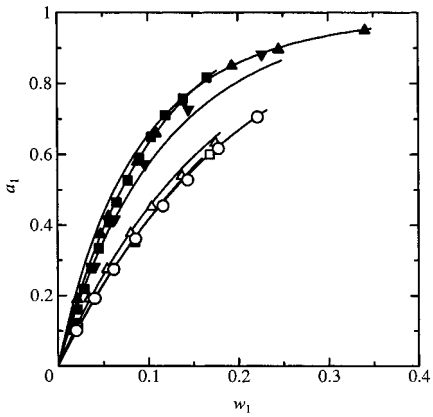


**Figure 5.** Activity of solvent $a_1$ vs solvent mass fraction $w_1$ in solvent + poly(vinyl acetate) systems at 333.2 K: ▲, methanol (1) + poly(vinyl acetate) (2); ■, ethanol (1) + poly(vinyl acetate) (2); ▼, 2-methyl-1-propanol (1) + poly(vinyl acetate) (2); △, acetone (1) + poly(vinyl acetate) (2); □, methyl ethyl ketone (1) + poly(vinyl acetate) (2); ○, propyl acetate (1) + poly(vinyl acetate) (2); lines, calculated with the UNIQUAC equation.

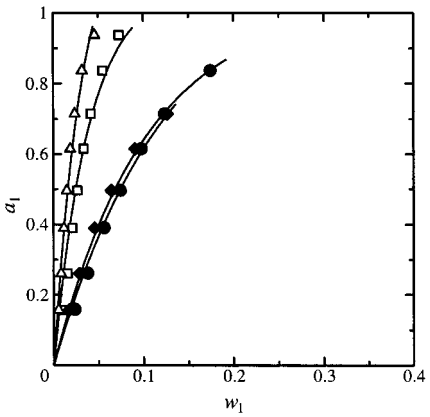


**Figure 6.** Activity of propanol $a_1$ vs solvent mass fraction $w_1$ at 333.2 K: □, propanol (1) + *cis*-1,4-polyisoprene (2); △, propanol (1) + polyisobutylene (2); ◆, propanol (1) + poly(*n*-butyl methacrylate) (2); ●, propanol (1) + poly(vinyl acetate) (2); lines, calculated with UNIQUAC equation.

interaction parameters. The best-fit UNIQUAC parameters, temperature range, and AAD between measured and calculated activities are summarized in Table 13. The overall AAD was 5.0% for all of the systems studied here. Comparisons between experimental data and correlation results are included in Figures 2−6. The temperature-independent parameters obtained in this work will be convenient in engineering applications, because they will allow solvent activities to be calculated accurately at various temperatures using one set of parameters.

## Conclusion

Solubility data for 11 polar organic solvents (methanol, ethanol, propanol, 2-propanol, butanol, 2-butanol, 2-methyl-1-propanol, acetone, methyl ethyl ketone, methyl acetate, and propyl acetate) in four polymers [*cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate)] were measured at (293.2, 313.2, 333.2, and 353.2) K by a piezoelectric quartz crystal microbalance apparatus. The polar solvents were more soluble in polar polymers than in nonpolar polymers, and the solubility of each solvent studied appeared to be lowest in polyisobutylene. Solvent activities were correlated using the UNIQUAC equation with an overall AAD of 5.0%.

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