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Physical Properties of Binary Mixtures of 3-Propylsydnone–Tetrahydrofuran and 1,2-Dimethoxyethane

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The physical properties of binary mixtures of 3-propylsydnone (3-PSD)–tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) at various temperatures were investigated in terms of the dielectric constant (ε), refractive index (n_D), density (ρ), and viscosity (η) measurements. The dielectric constants of these binary mixtures gradually decrease with increasing THF and DME mole fractions (X_{THF} and X_{DME}). The dielectric constant data can be described by a cubic equation of the THF and DME mole fractions. The n_D of these binary mixtures decreases linearly with increasing temperature. A linear relationship exists between the density and the temperature at each X_{THF} and X_{DME}. The η of these binary mixtures rapidly decrease with increasing X_{THF} and X_{DME} at low temperature. The excess viscosity (η^E) of the mixtures is negative over the entire THF and DME mole fractions, and has a maximum value at 0.4 X_{THF} and X_{DME}. The negative value of η^E may be taken as the formation of weakly associated compounds. It was found from the ^{1}H and ^{17}O NMR spectra that the interaction in a 3-PSD–THF mixture occurs highly between the hydrogen of the 4-position in the sydnone ring and the oxygen of the THF molecule. From the η^E and NMR spectra it seems that one of the associated compounds due to weak hydrogen bonding in these binary mixtures is formed at the 0.4 THF and DME mole fractions. The interactions in these binary mixtures were investigated on the basis of the activation parameters by using the Eyring rate equation. The activation enthalpy (ΔH^*_η) gradually increases with increasing viscosity of the mixtures. It is considered that the mechanism of viscous flow for these binary mixtures is a thermally activated single process. The activation entropy (ΔS^*_η) gradually changes from positive to negative with increasing X_{THF} and X_{DME}. It seems that the change of sign in ΔS^*_η near to 0.4 THF and DME mole fractions depends on the formation of weakly associated compounds at that mole fraction. The activation Gibbs energy (ΔG^*_η) with a positive ΔS^*_η value gradually decreases with increasing temperature. On the contrary, the ΔG^*_η with a negative ΔS^*_η value gradually increases with increasing temperature. This means that the change in ΔS^*_η greatly contributes to that of ΔG^*_η.

In previous papers[1,2] we reported on the physical properties of some 3-alkylsydnones. The 3-propylsydnone (3-PSD) is a liquid at room temperature and has a large dipole moment, high dielectric constant of more than 90, compared with those of other aprotic solvents at 25 °C. However, it is preferable to use a 3-PSD and low viscosity solvent mixture as a good solvent for the electrolyte, due to the high viscosity of 3-PSD.

The purpose of the present study is to elucidate the bulk physical properties, such as the dielectric constant, refractive index, density, and viscosity of binary mixtures of 3-PSD–tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). In addition, the interactions between 3-PSD and these ether solvents were considered on the basis of the NMR spectra and activation parameters of viscous flow for these binary mixtures.

Experimental

General. The measurement of the dielectric constant was taken on a Hewlett Packard 4192A LF impedance analyzer equipped with a thermostat. The frequency used was 1 MHz. The apparatus and techniques for measurements of the refractive index, density, and viscosity were similar to those previously used.[2] The NMR spectra were measured with JEOL-90Q and 400WB spectrometers.

Materials. The preparation, purification, and confirmation for the formation of 3-propylsydnone (3-PSD) have been described elsewhere.[2,3] Commercial tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were purified by refluxing overnight with lithium aluminum hydride and fractionally distilling.[4] Each solvent was dehydrated by purified molecular sieves (4A) before preparation of the solutions.

Results and Discussion

The dielectric constant (ε) for binary mixtures of 3-propylsydnone (3-PSD)–tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) gradually decreases with increasing THF and DME mole fractions (X_{THF} and X_{DME}), as shown in Fig. 1. The decrease in the dielectric constant is related to the arrangement of the permanent dipole in the mixture to be prevented by the thermal motion of the molecule due to an increase in the temperature. The loose decrease of the dielectric constants with increasing X_{THF} and X_{DME} in Fig. 1 is different from an abrupt decrease of those for dimethyl sulfoxide–water, N,N-dimethylformamide–water,[5,6] and acetonitrile–water[5] mixtures with strong interactions, the formation of associated complexes due to hydrogen bonding. This fact implies that the interaction (association) between 3-PSD and THF and DME is very small. In Fig. 1 it seems that 3-PSD–DME mixture behaves rather ideally. The dielectric constant data of the mixtures can be described as the following functions of the THF and DME mole fractions:

$$\varepsilon = 93.11 - 52.79X_{THF} - 41.54X_{THF}^2 + 8.78X_{THF}^3, \quad (1)$$

$$\varepsilon = 92.86 - 77.48X_{DME} - 10.65X_{DME}^2 + 2.41X_{DME}^3. \quad (2)$$

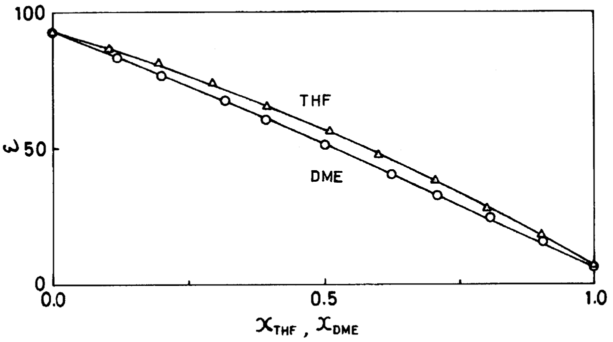

Fig. 1. Dielectric constant (ε) dependence on the mole fraction of tetrahydrofuran (X_{THF}) and 1,2-dimethoxyethane (X_{DME}) for binary mixtures of 3-propylsydnone (3-PSD)–THF and DME.

The maximum deviation between the experimental and calculated values for Eqs. 1 and 2 was found to be below 1.2 and 0.8%, respectively. By using Eqs. 1 and 2 it is possible to accurately calculate the dielectric constants of the mixtures at any mole fraction. Figure 2 shows the change in the refractive index (n_{D}) with X_{THF} of the 3-PSD–THF mixture at various temperatures. The n_{D} gradually decreases, in analogy with ε, with increasing X_{THF} at any temperature. On the other hand, the change of n_{D} for each X_{THF} with temperature in the 3-PSD–THF mixture is shown in Fig. 3. In general, the n_{D} of many single solvents, except for water,[4] decreases linearly with increasing temperature.[7] In Fig. 3, it is shown that the change in n_{D} for the 3-PSD–THF mixture has a similar behavior to that of the single solvent. The change of n_{D} with X_{DME} and the temperature for the 3-PSD–DME mixture was analogous to that for the 3-PSD–THF mixture.

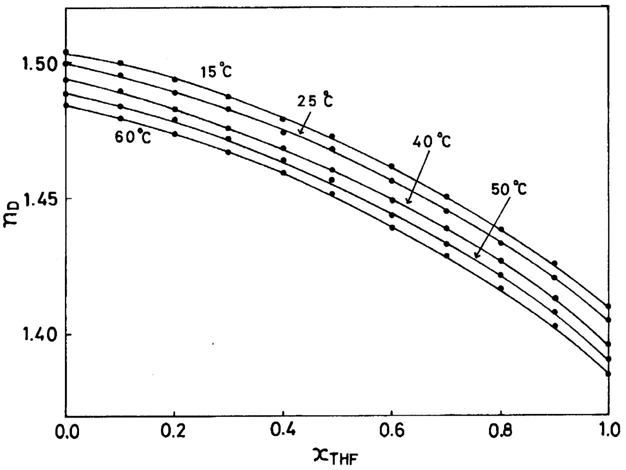

Fig. 2. Refractive index (n_{D}) dependence on the THF mole fraction of a 3-PSD–THF mixture at various temperatures.

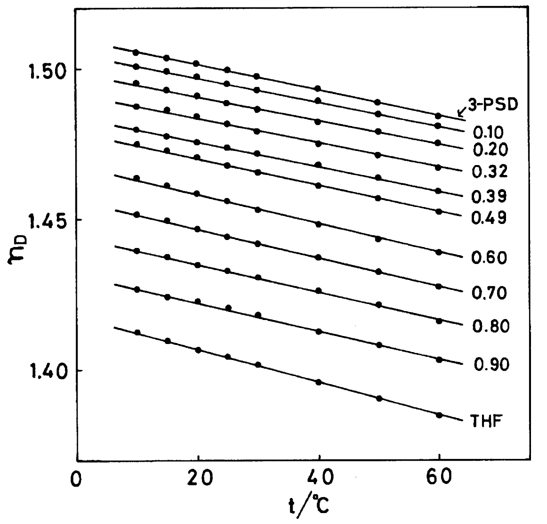

Fig. 3. Temperature dependence on the refractive index of a 3-PSD–THF mixture. The numerical value on each line indicates the THF mole fraction.

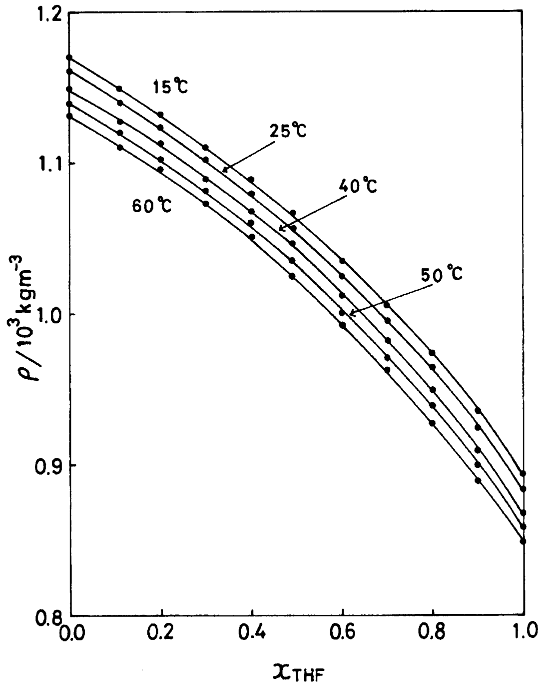

Fig. 4. Density (ρ) of the 3-PSD–THF mixture as a function of the THF mole fraction at various temperatures.

The density (ρ) data for the 3-PSD–THF mixture at various temperatures are given in Fig. 4. The change in the density given in Fig. 4 supports that of the refractive index in Fig. 2, since the refractive index generally depends on the density of the mixture. The linear relationships shown in many single solvents, for example, dimethyl sulfoxide,[8,9] N,N-dimethylformamide,[10—12] propylene carbonate, and hexamethylphosphoric triamide,[13] were observed between the density and the temperature at each THF and DME mole fraction (Fig. 5). The viscosity (η) data of these binary mixtures were calculated from the density data. Figure 6 shows the change in the viscosity in the 3-PSD–THF

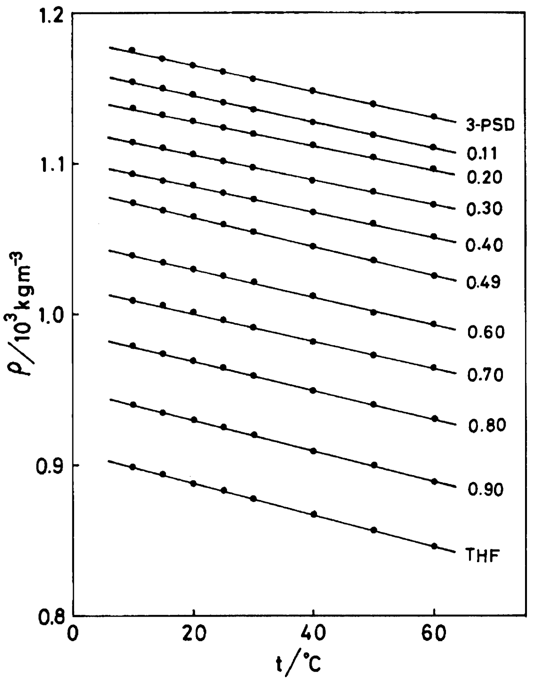

Fig. 5. Temperature dependence on the density of the 3-PSD–THF mixture. The numerical value on each line indicates the THF mole fraction.

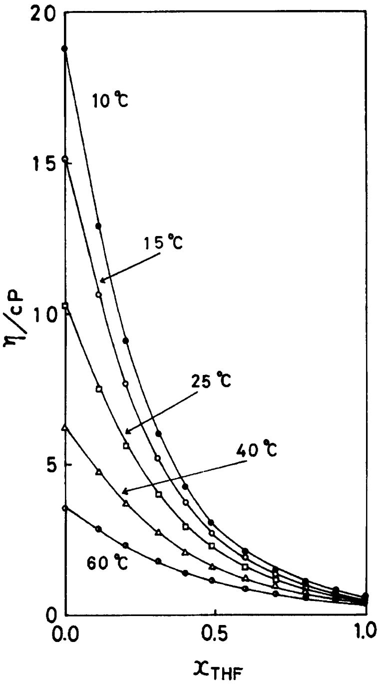

Fig. 6. Viscosity (η) of the 3-PSD–THF mixture as a function of the THF mole fraction at various temperatures.

mixture with increasing THF mole fraction at each temperature. The difference in the viscosity with X_{THF} at high temperature becomes smaller. No change in the viscosity, even at lower temperatures (Fig. 6), indicates in a way similar to the density a salient form observed in highly associated complexes with strong hydrogen bonding, such as alcohol–water, *N*,*N*-dimethylformamide–water,[6,10,11] and dimethyl sulfoxide–water[14,15] mixtures. It is considered that the interaction between 3-PSD and THF and DME is very small. In addition, the viscosity data with X_{THF} and X_{DME} are consistent with those of the dielectric constants. Figures 7 and 8 show the excess viscosity (η^{E}) of these binary mixtures at 10, 25, and 40 °C. The η^{E} values become higher at 10 °C in Figs. 7 and 8, since these binary mixtures behave much like a nonideal mixture at low temperature. The η^{E} values are negative over the entire range of THF and DME mole fractions, as shown in Figs. 7 and 8. The negative η^{E} may be taken as the formation of weakly

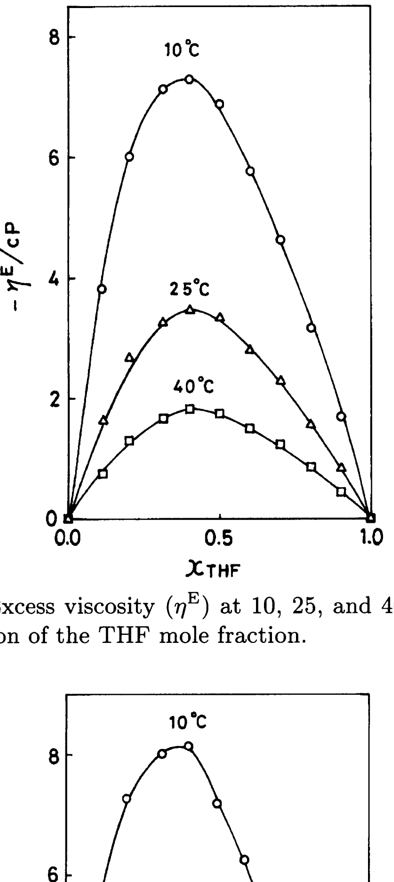

Fig. 7. Excess viscosity (η^{E}) at 10, 25, and 40 °C as a function of the THF mole fraction.

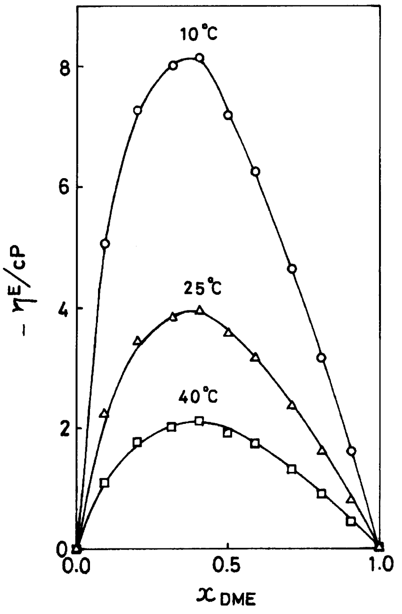

Fig. 8. Excess viscosity at 10, 25, and 40 °C as a function of the DME mole fraction.

associated compounds due to the predominance of dispersion and dipole–induced dipole interactions (van der Waals force).[16)] The maximum η^E values are 0.4 THF and DME mole fractions at any temperature. Accordingly, it is assumed that the interaction between 3-PSD and DME takes place significantly at 0.4 THF and DME mole fractions. Further, it seems that one of the weakly associated compounds shown at least below is formed at 0.4 THF and DME mole fractions.

$$2(\text{3-PSD}) + 3\text{THF} \text{ or } 3\text{DME} \rightleftarrows \text{Compounds}$$

The interaction between the 3-PSD and THF molecules was studied in terms of the ^{1}H and ^{17}O NMR spectra. Figure 9 shows the chemical shifts of protons (^{1}H nuclei) for the 3-PSD–THF mixture. The chemical shift of the number-4 proton (4-position of the sydnone ring) is most significantly observed in comparison with those of other protons. On the other hand, no chemical shift for every proton in the THF and DME molecules was observed at any THF and DME mole fraction. Furthermore, for example, in the spectra of ^{17}O NMR for the mixed solvents of 0.5 X_{THF} and X_{DME}, a 0.45 ppm downfield chemical shift was observed in comparison with that of the ^{17}O NMR spectra for pure THF and DME. Consequently, it was found that the interaction (weak association or weak hydrogen bonding) of 3-PSD with THF and DME occurs significantly between the oxygen of THF and DME and the number-4 proton of the 3-PSD molecule.

The interaction between 3-PSD and THF and DME by using the Eyring rate equation[17,18)] shown in Eq. 3 or Eq. 3a was investigated from the

$$\eta_{\mathrm{mix}} = \frac{Lh}{V}\exp\left[-\frac{\Delta S^*_\eta}{R}\right]\ \exp\left[\frac{\Delta H^*_\eta}{RT}\right] \tag{3}$$

$$\log\frac{\eta_{\mathrm{mix}}V}{Lh} = -\frac{\Delta S^*_\eta}{2.303R} + \frac{\Delta H^*_\eta}{2.303R}\frac{1}{T} \tag{3a}$$

activation parameters, such as the enthalpy (ΔH^*_η), entropy (ΔS^*_η), and Gibbs energy (ΔG^*_η) of viscous flow for these binary mixtures, where η_{mix} is the viscosity of the mixture, h Plank's constant, L Avogadro's constant, V the molar volume, and R the gas constant. For example, plots of log η_{mix} vs. $1/T$ at each X_{THF} for the 3-PSD– THF mixture yield straight lines (Fig. 10). The ΔH^*_η and ΔS^*_η values were obtained from the slope and intercept of the straight lines. The activation Gibbs energy was calculated from the ΔH^*_η and ΔS^*_η values. Tables 1 and 2 show the activation parameters of viscous flow for these binary mixtures. The ΔH^*_η corresponds to the activation energy for viscous flow. The ΔH^*_η for the mixtures gradually increases with increasing viscosity (Tables 1 and 2). No maximum ΔH^*_η value shown in the system with highly associated complexes, due to strong hydrogen bonding, such as hexamethylphosphoric triamide–water mixture,[18)] was observed for these binary mixtures. Accordingly, it is considered that the association in these binary mixtures is very small. In addition, one may suggest that the mechanism of viscous flow for these binary mixtures is a thermally activated single process. Regarding the ΔS^*_η values, these gradually change from positive to negative with increasing X_{THF}, and X_{DME}. The ΔS^*_η values of 3-PSD, THF, and DME (calculated similarly by using Eq. 3a) are 19.76, −12.77, and −15.61 J mol^{-1} deg^{-1}, respectively. The positive value for 3-PSD reflects that the disorder-

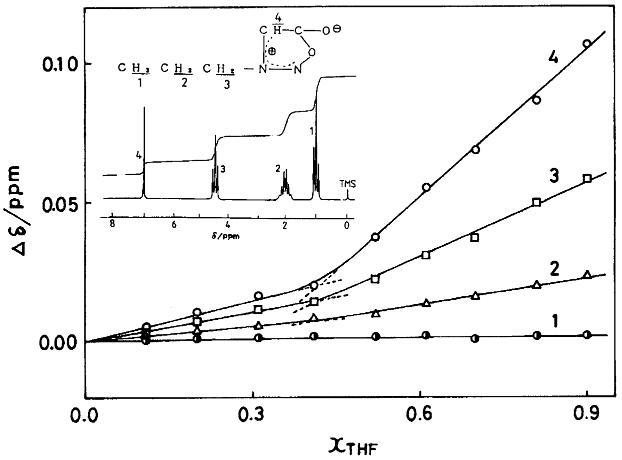

Fig. 9. Chemical shift ($\Delta\delta = \delta_{\text{3-PSD}} - \delta_{\mathrm{mix}}$) for the ^{1}H NMR spectrum of the 3-PSD–THF mixture. The numbers in the spectrum were assigned to those of protons in the 3-PSD molecule. The chemical shifts for the triplet of the number-1 and -2 protons were calculated by using the center one in three peaks. The chemical shift of the number-2 proton was calculated by using the mean value of the central two peaks.

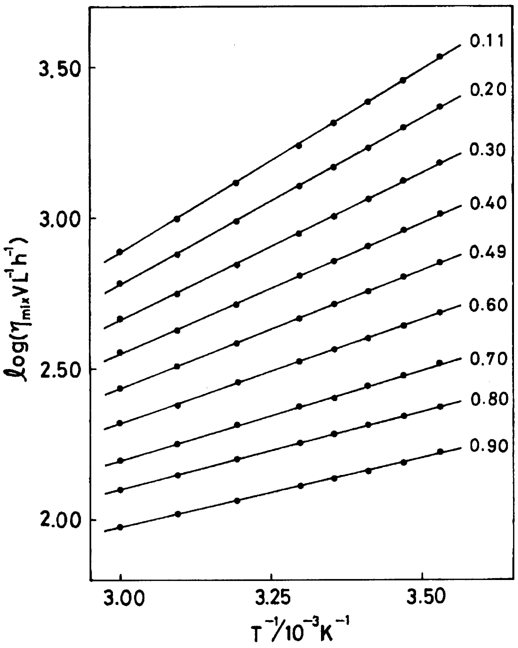

Fig. 10. Plot of the logarithm of $\eta_{\mathrm{mix}}\,V/Lh$ vs. $1/T$ for 3-PSD–THF mixture. The numerical value on each line indicates the THF mole fraction.

Table 1. Activation Parameters of Viscous Flow for 3-PSD–THF Mixture

X_{THF}	ΔH_η^*	ΔS_η^*	ΔG_η^*/kJ mol^{-1}							
	kJ mol^{-1}	J mol^{-1} K^{-1}	10 °C	15 °C	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C
0.11	23.16	14.32	19.10	19.03	18.96	18.89	18.81	18.67	18.53	18.38
0.20	21.11	10.15	18.23	18.18	18.13	18.08	18.03	17.93	17.82	17.72
0.30	18.66	5.11	17.21	17.19	17.16	17.13	17.11	17.06	17.01	16.96
0.40	16.64	1.16	16.31	16.30	16.30	16.29	16.29	16.28	16.26	16.25
0.49	14.99	−1.59	15.44	15.45	15.46	15.46	15.47	15.49	15.50	15.52
0.60	13.12	−5.01	14.54	14.57	14.59	14.62	14.64	14.69	14.74	14.79
0.70	11.43	−7.73	13.62	13.66	13.70	13.74	13.78	13.85	13.93	14.01
0.80	9.92	−10.44	12.87	12.93	12.98	13.03	13.08	13.19	13.29	13.40
0.90	8.38	−12.72	11.98	12.05	12.11	12.17	12.24	12.36	12.49	12.62

Table 2. Activation Parameters of Viscous Flow for 3-PSD–DME Mixture

X_{DME}	ΔH_η^*	ΔS_η^*	ΔG_η^*/kJ mol^{-1}							
	kJ mol^{-1}	J mol^{-1} K^{-1}	10 °C	15 °C	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C
0.09	22.08	10.95	18.98	18.92	18.87	18.81	18.76	18.65	18.54	18.43
0.20	20.02	7.40	17.92	17.88	17.85	17.81	17.77	17.70	17.62	17.55
0.31	17.49	2.18	16.87	16.86	16.85	16.84	16.83	16.81	16.79	16.76
0.41	15.70	−1.04	16.00	16.00	16.01	16.01	16.02	16.03	16.04	16.05
0.50	13.91	−4.43	15.16	15.18	15.20	15.23	15.25	15.29	15.34	15.38
0.59	12.55	−6.47	14.38	14.41	14.45	14.48	14.51	14.58	14.64	14.71
0.71	10.55	−10.38	13.49	13.55	13.60	13.65	13.70	13.81	13.91	14.01
0.81	9.49	−11.71	12.81	12.87	12.93	12.99	13.04	13.16	13.28	13.40
0.91	8.15	−13.84	12.07	12.14	12.21	12.28	12.35	12.48	12.62	12.76

ing process between the species taking part in the flow process is greatest compared with that of the mixtures, THF and DME. In addition, it seems that the change of the sign in ΔS_η^* from positive to negative at near to 0.4 X_{THF} and X_{DME} depends on the formation of weakly associated compounds at that mole fraction. The activation Gibbs energy (ΔG_η^*) with positive ΔS_η^* value gradually decreases with increasing temperature. On the contrary, the ΔG_η^* with negative ΔS_η^* value gradually increases with increasing temperature. This means that the change of ΔS_η^* greatly contributes to that of ΔG_η^*.

In conclusion, weakly associated compounds due to weak hydrogen bonding are formed in binary mixtures of 3-PSD–THF and DME. It was found that the higher is the viscosity of the mixture, the larger are the activation parameters. The activation enthalpy gradually changes from positive to negative with increasing THF and DME mole fractions. The change in the activation Gibbs energy with temperature is reversed by the sign of the activation entropy of these binary mixtures.

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