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SOLUBILITY PARAMETERS OF LIQUID CRYSTALS

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Solubility parameters are introduced for the first time to investigate the solubility problem of liquid crystals. Using Fedors method that is used for polymers and organic solvent gives solubility parameters of liquid crystals in the range of 8.0 $(cal/cm^3)^{1/2}$ to 11.0 $(cal/cm^3)^{1/2}$. Polar liquid crystal compounds have large solubility parameters compared with nonpolar ones. Moreover, an aromatic ring, which is frequently encountered in liquid crystal compounds, increases the solubility parameter value. Since these parameters can be used to calculate the activity coefficient in regular solution theory, we attempted to investigate the solubility of solids and gases for two types of liquid crystal solvents, namely a polar nematic liquid crystal solvent and a nonpolar one. We found that the solvent dependence could be explained by the solubility parameter difference between a solute and a nematic liquid crystal solvent.

Keywords: solubility parameter; solubility; activity coefficient; regular solution; nematic liquid crystal solvent

INTRODUCTION

The solubility parameters of liquids and polymers have been widely used to investigate not only thermodynamic problems of solutions [1] but also physical properties such as surface tension [2] and wettability [3]. Therefore, it is interesting to introduce such parameters into the study of liquid crystal compounds. As reviewed by Weiss [4], liquid crystal can serve as an anisotropic solvent for investigating a chemical reaction mechanism and for controlling the chemical reaction itself. Although the solubility of a solute in a liquid crystal solvent is an important factor, this solubility problem has

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attracted less attention. We have reported about acetylene polymerization in a nematic liquid crystal solvent in order to obtain an aligned polyacetylene film [5–7]. In those studies, we did not answer basic questions on the solubility of acetylene and the Ziegler-Natta catalyst in the liquid crystal solvent. In addition, solubility problem for liquid crystals is an area of current interest in display applications. For example, a wide temperature range of the nematic state in a liquid crystal display can be obtained by using an eutectic mixture for which composition and temperature are calculated as a solubility problem of a solid. So far, these calculations have been done by the well-known Schröder-van Laar equation [8–10]. However, this equation is limited to ideal systems.

With this in mind, we attempted to apply solubility parameters to obtaining the solubility of solids and gases in a nematic liquid crystal solvent. Solubility parameters of liquid crystals are used to calculate the activity coefficient in the regular solution theory, which is one thermodynamic treatment for a nonideal system [2]. We first estimate the solubility parameters of liquid crystal compounds by Fedors method, which has been widely used for polymers and organic solvents [11]. This method requires only a knowledge of the chemical structure of the liquid crystals. Then, the solubility of solids and gases in a nematic solvent can be discussed from the viewpoints of molecular structure of liquid crystal compounds.

EXPERIMENTAL

Materials

Three liquid crystal compounds and a liquid crystal mixture were used as received: Trans-4-propyl-(4-ethoxylphenyl)-cyclohexane (ZLI-1476), trans-4-propyl-(4-buthoxylphenyl)-cyclohexane (ZLI-1477), and a mixture (ZLI-1083) of trans-4-propyl-(4-cyanolphenyl)-cyclohexane, trans-4-pentyl-(4-cyanolphenyl)-cyclohexane, and trans-4-heptyl-(4-cyanolphenyl)-cyclohexane were obtained from Merck Japan Ltd. BDH Ltd. provided 4-Cyano-4-ethylbiphenyl (K6). Two nematic liquid crystal solvents were used: ZLI-1083 by itself and a mixture of ZLI-1476 and ZLI-1477.

Measurements

The calorimetric curves were recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter during the processes of heating and cooling. The heating rate was 5°C/min. The temperatures and heat capacity were calibrated with the melting point and the latent heat of melting indium (156.6°C,13.8 kcal/mol). The molar fraction in a nematic liquid crystal mixture was measured with a Hitachi G-5000 gas chromatograph equipped

with flame ionization detector. The solubility of oxygen and nitrogen in a nematic liquid crystal solvent was measured with a Hitachi Type-163 gas chromatograph equipped with a thermal conductivity detector.

RESULTS AND DISCUSSION

Solubility Parameters of Liquid Crystal Compounds

The solubility parameter of a liquid, δ, is defined as the square root of the cohesive energy density. Since the cohesive energy density itself is defined as the ratio of the energy of vaporization (ΔE) to the molar volume (V), δ is written as follows:

$$\delta = (\Delta E/V)^{1/2} \tag{1}$$

In this paper, we only deal with the solubility parameters of the nematic liquid crystal phase. The enthalpy and molar volume changes of the nematic liquid crystal-isotropic liquid transition are negligibly low compared with those of the nematic liquid crystal-solid transition [12,13]. Therefore, the solubility parameter defined in Equation (1) can be applied to a nematic liquid crystal as well as an isotropic liquid.

According to Fedors method [11], ΔE and V can be estimated simply by assuming

$$\Delta E = \sum \Delta e_i \tag{2}$$

and

$$V = \sum \Delta v_i \tag{3}$$

where Δe_i and Δv_i are the additive atomic and group contributions for the energy of vaporization and molar volume, respectively. Table 1 gives values of Δe_i and Δv_i for groups frequently encountered in liquid crystal compounds which allow estimation of the solubility parameters of a great number of liquid crystal compounds. However, the values for a cyano group attached to an aromatic ring were not reported by Fedors. In this work, we use Δe_i and Δv_i of a nitro group attached to an aromatic ring as values of a cyano group, because benzonitrile has almost the same solubility parameter as nitrobenzene [1].

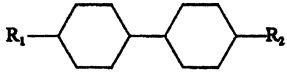
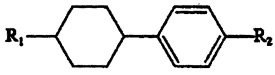
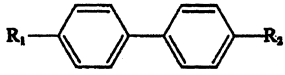
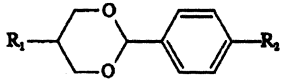
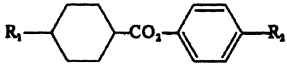
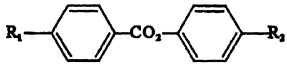
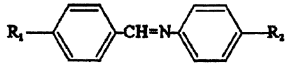
The solubility parameters of typical liquid crystal compounds are listed in Table 2. As shown in CCH and PCH derivatives, polar compounds have large solubility parameters compared with nonpolar ones. The order of solubility parameters for cyano derivatives is:

$$\text{CCH-3} < \text{PCH-3} < \text{PDX-3} < \text{BC-3}$$

TABLE 1 Atomic and Group Contributions to Energy of Vaporization and Molar Volume at 25°C

Atom or group	Δe(cal/mol)	Δv(cm^3/mol)
Phenyl	7630	71.4
Phenyl (disubstituted)	7630	52.4
Phenyl (trisubstituted)	7630	33.4
Phenyl (tetrasubstituted)	7630	14.4
Cyclohexyl (disubstituted)	6610	78.4
Dioxane (disubstituted)	5850	53.8
-CH_3	1125	33.5
-CH_2-	1180	16.1
-O-	800	3.8
-CN (aromatic)	3670	32.0
-NO_2 (aromatic)	3670	32.0
-Cl (aromatic)	2208	28.0
-F (aromatic)	800	22.0
-CH_2-CH_2-	2360	32.2
-CH=CH-	2060	27.0
-C≡C-	3380	13.0
-CH = N-	3830	18.5
-COO-	4300	18.0

TABLE 2 The Solubility Parameters and Molar Volumes of Liquid Crystal Compounds

Compound	Symbol	R_1	R_2	$\delta((cal/cm^3)^{1/2})$	V(cm^3/mol)
	CCH-33	C_3H_7	C_3H_7	8.37	288.2
	CCH-302	C_3H_7	OC_2H_5	8.47	275.9
	CCH-3	C_3H_7	CN	9.62	246.5
	PCH-33	C_3H_7	OC_2H_5	8.99	262.2
	PCH-302	C_3H_7	OC_4H_9	9.13	249.9
	PCH-3	C_3H_7	CN	9.68	228.5
	BC-3	C_3H_7	CN	10.52	202.5
	PDX-3	C_3H_7	CN	10.06	203.9
	ECH-3	C_3H_7	CN	10.21	246.5
	ER-3	C_3H_7	CN	11.01	220.5
	MBBA	CH_3	C_4H_9	10.29	242.4

This trend indicates that an aromatic ring increases the solubility parameter value. The large solubility parameter of MBBA, which is well known as a standard room-temperature liquid crystal, is due to the presence of two phenyl groups. The introduction of ester groups into liquid crystal compounds also increases the solubility parameter:

$$\text{PCH-3} < \text{ECH-3 and BC-3} < \text{ER-3}$$

The range of solubility parameters for organic solvents is wide with values from 7.4 $(\text{cal/cm}^3)^{1/2}$ to 14.5 $(\text{cal/cm}^3)^{1/2}$ [1]. A large solubility parameter is due to the presence of organic solvents with hydroxyl groups. The solubility parameters of ethyl alcohol and methyl alcohol are 12.7 $(\text{cal/cm}^3)^{1/2}$ and 14.5 $(\text{cal/cm}^3)^{1/2}$, respectively. Consequently, the solubility parameters for liquid crystals are in the same range as organic solvents other than alcohols.

Solubility Parameters of Liquid Crystal Mixtures

Since liquid crystal compounds show hardly any nematic state at room temperature, it is useful to estimate the solubility parameter for a nematic liquid crystal mixture. Estimations have already been investigated for polymers and organic solvents [1], and the same procedure is used to calculate the solubility parameter of a mixture of liquid crystal compounds.

According to the literature, an additive rule can be applied to obtain the solubility parameter of a nematic liquid crystal mixture [1]. The solubility parameter for a mixture with N components, δ, is defined as follows:

$$\delta = \sum_{i=1}^{N} \phi_i \delta_i \tag{4}$$

where δ_i is the solubility parameter of the i component. ϕ_i is the volume ratio of the i component and is defined as follows:

$$\phi_i = \frac{X_i V_i}{\sum_{i=1}^{N} X_i V_i} \tag{5}$$

Consequently, the solubility parameter of a mixture can be calculated if we know the solubility parameter (δ_i), molar fraction (X_i), and the molar volume (V_i) of the components comprising the mixture.

Solubility parameters of two liquid crystal solvents, which are in the nematic state at room temperature, are listed in Table 3. The first nematic solvent is a nonpolar mixture of trans-4-propyl-(4-ethoxylphenyl)-cyclohexane and trans-4-propyl-(4-buthoxylphenyl)-cyclohexane. The

TABLE 3 The Solubility Parameters of Nematic Liquid Crystal Mixtures at 25°C

			Component		Mixture	
System	Composition	Molar%	$\delta((\text{cal/mol})^{1/2})$	$V(\text{cm}^3/\text{mol})$	$\delta((\text{cal/mol})^{1/2})$	$V(\text{cm}^3/\text{mol})$
Nematic A	PCH-302	54	9.13	249.9	9.10	264.7
	PCH-304	46	9.07	282.1		
Nematic B	PCH-3	33	9.68	228.5	9.55	258.5
	PCH-5	41	9.55	260.7		
	PCH-7	26	9.44	292.9		

other is a polar mixture of trans-4-propyl-(4-cyanolphenyl)-cyclohexane, trans-4-pentyl-(4-cyanolphenyl)-cyclohexane, and trans-4-heptyl-(4-cyanolphenyl)-cyclohexane. Hereafter, the mixtures are called Nematic A and Nematic B, respectively. Nematic A is nonpolar and its solubility parameter is 9.10 $(\text{cal/cm}^3)^{1/2}$. Nematic B is polar and its solubility parameter is 9.55 $(\text{cal/cm}^3)^{1/2}$. As expected, Nematic B has a larger solubility parameter than Nematic A. The nematic liquid crystal-isotropic transition temperatures of Nematic A and Nematic B are 34 and 54°C, respectively.

Solubility of Solids in Nematic Liquid Crystal Solvent

To treat solubility problems of solids in nematic liquid crystal, it is important to estimate the solubility of the polar liquid crystal compound in nonpolar liquid crystal solvent, because polar liquid crystal compounds tend to be in the solid state at room temperature. For this reason, 4-cyano-4-ethylbiphenyl, BC-2 (Table 2), is selected as the polar solid. Its solubility parameter is 10.7 $(\text{cal/cm}^3)^{1/2}$. The melting point and the latent heat of melting of 4-cyano-4-ethylbiphenyl are 75°C and 4150 cal/mol, respectively. The nematic liquid crystal-isotropic transition temperature of the compound is obtained as 22°C by extrapolation. Therefore, the dissolution of 4-cyano-4-ethylbiphenyl in nematic liquid crystal solvent results in the nematic state of the solvent at room temperature. Nematic A and Nematic B are used as nematic liquid crystal solvents in these experiments.

Nematic liquid crystal-solid transition curves in regular solution are described by Equation (6) [2]:

$$\ln(\gamma_1 \cdot X_1) = -\frac{\Delta H_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) \tag{6}$$

where ΔH_1 is transition enthalpy at the melting temperature T_1 (K) of solid solute. In this work, the solid solute is 4-cyano-4-ethylbiphenyl (BC-2), T is the temperature of the solubility measurement, γ_1 is the activity

coefficient, and X_1 is the molar fraction of a solid solute. In regular solution theory, the activity coefficient is defined as follows [2]:

$$\ln \gamma_1 = V_1(1-\phi_1)^2(\delta_1-\delta_2)^2/RT \tag{7}$$

where δ_1 and δ_2 are solubility parameters of a solid solute and a nematic liquid crystal solvent, respectively. From Equations. (5)–(7) we obtain

$$T = \frac{\Delta H_1 + V_1\left(\frac{(1-X_1)V_2}{X_1V_1+(1-X_1)V_2}\right)^2(\delta_1-\delta_2)^2}{\frac{\Delta H_1}{T_1} - R\ln X_1} \tag{8}$$

From Equation (8), nematic liquid crystal-solid transition temperatures (T) are calculated for all molar fractions of the solid solute (X_1). Consequently, when we want to know the solubility of a solid solute at room temperature (25°C), we only need to find the molar fraction where T equals room temperature. If δ_1 equals δ_2, Equation (8) is reduced to the well-known Schröder-van Laar equation. As shown in Table 3, a homologue series of liquid crystal compounds tends to be in the same range of solubility parameters. If δ_1 nearly equals δ_2, the term $(\delta_1-\delta_2)^2$ becomes negligibly low and can be treated as zero. This is the reason why the Schröder-van Laar equation is limited to a homologue series of liquid crystal compounds [8].

The solubility of 4-cyano-4-ethylbiphenyl in nematic solvent is measured by gas chromatography analysis for the saturated nematic solution of 4-cyano-4-ethylbiphenyl at 25°C. The calibration of the molar fraction is done by using the unsaturated solution, including a given concentration of 4-cyano-4-ethylbiphenyl. The measured solubility for two nematic solvents is listed with the values calculated by Equation (8) in Table 4. For comparison, the values calculated using the Schröder-van Laar equation are also listed in Table 4 as ideal solubility. We can see that the measured values are closer to the values calculated as a regular solution than calculated as an ideal solution. Moreover, we note that the solubility of BC-2 differs between the two nematic solvents. The solubility behavior cannot be interpreted by

TABLE 4 The Solubility of Solid into Nematic Liquid Crystal Solvents at 25°C

System		$\delta((\text{cal/mol})^{1/2})$		$V(\text{cm}^3/\text{mol})$		Solubility (molar fraction)		
						Calculated		
Host	Guest	Host	Guest	Host	Guest	Ideal	Regular	Measured
Nematic A	BC-2	9.10	10.67	264.7	186.4	0.37	0.21	0.23
Nematic B	BC-2	9.55	10.67	258.5	186.4	0.37	0.29	0.32

the Schröder-van Laar equation, and it coincides with our experience that a polar solid is more soluble in polar solvent than in nonpolar solvent. These results show solubility parameters are a useful tool for such calculation, and they make it possible to discuss the solid solubility from the molecular structure of liquid crystals.

Solubility of Gases in Nematic Liquid Crystal Solvent

For simplicity in the solubility experiment, we deal with only the solubility of oxygen and nitrogen in nematic liquid crystal solvent. According to regular solution theory, the solubility of gases in a solvent at one atmosphere pressure is defined as follows [2]:

$$X_1 = 1/(P_1^0(\exp(V_1(\delta_1 - \delta_2)^2/RT)) \tag{9}$$

where X_1 and V_1 are molar fraction and molar volume of a gas, and δ_1 and δ_2 are solubility parameters of a gas and a nematic solvent, respectively. P_1^0 is saturated pressure of a gas, and its value has been reported as fugacity by Prausnitz [14].

The solubility of gases is measured by gas chromatography for the nematic solvent kept at 25°C. For example, the solubility of oxygen at one atmosphere pressure is easily calculated by means of partial pressures of oxygen in air. The two nematic solvents used are nematic A and B. The measured solubility for them is listed in Table 5 together with the values calculated by Equation (9). As expected from the solid solubility results, the solubility of gases also depends on the differences in the solubility parameters. Because the solubility parameter of oxygen is larger than that of nitrogen, it is reasonable that the solubility of oxygen in nematic solvent is larger than that of nitrogen. Moreover, we find that the differences in the solubility parameters of the two nematic solvents clearly affect the solubility of gases. The gas solubility behavior also indicates that solubility parameters are useful for studying liquid crystals. The solubility parameters of organic gases are much larger among gases. For example, the

TABLE 5 The Solubility of Gases into Nematic Liquid Crystal Solvents

		Properties of gas		Molar fraction ($\times 10^{-4}$)	
System	$P_1^0(10^5\text{Pa})$	$\delta((\text{cal/mol})^{1/2})$	$V(\text{cm}^3/\text{mol})$	Calculated	Measured
Nematic A-O_2	252	4.0	33.0	9.3	11.1
Nematic A-N_2	237	2.6	32.4	4.1	6.0
Nematic B-O_2	252	4.0	33.0	7.1	8.2
Nematic B-N_2	237	2.6	32.4	3.0	4.3

solubility parameter of acetylene is about 6.0 $(cal/cm^3)^{1/2}$. This value means that acetylene gas is readily soluble in liquid crystal solvent. We now know that the formation of polyacetylene film in liquid crystal solvent is due to the large solubility of acetylene in liquid crystals.

CONCLUSION

Since regular solution theory is an approximate treatment for thermodynamics of solutions, it is unlikely that the calculated values completely agree with measured values. However, our present work showed that solubility parameters are an important factor for liquid crystal compounds as well as polymers and organic solvents. In this study, we relied on the Fedors method to estimate solubility parameters. The method is very simple and does not give highly accurate values for anisotropic molecules such as liquid crystal compounds. Consequently, we should measure the solubility parameters of liquid crystal compounds by experiments. In future work, we are planning to look at physical properties, such as the surface tension of liquid crystals.

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