Liquid crystal solutions at infinite dilution: Enthalpy–entropy compensation of solutes transfer properties between phases

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ABSTRACT

Careful gas chromatographic (GLC) studies provide thermodynamic data for insights into solution processes in non-volatile solvents. In this study, thermodynamic properties of solutes at infinite dilution of several liquid crystals measured by GLC were examined. The enthalpy and entropy of solutions in mesophases were positive and higher than those of isotropic stationary phases. When solute transfer enthalpy (ΔH_{tr}) and transfer entropy (ΔS_{tr}) between two phases of a liquid crystal were examined, remarkable enthalpy–entropy compensation relations were observed. This was because the small values of transfer free energy. Both ΔH_{tr} and $T\Delta S_{tr}$ had large values and were almost equal, resulting in small values of transfer free energy. The temperature dependency of the disorder parameter in Flory's theory of liquid crystals was used to explain high values of the enthalpy and entropy of solution.

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1. Introduction

Gas–liquid chromatography (GLC) has been applied for many years for measuring solute vapor solubility in non-volatile materials [1–3] as well as for other physico-chemical information [4–7]. The use of liquid crystals as stationary phases in GLC is also widely known. Analytical separation of stereoisomers, active and inactive geometric isomers, has been successfully carried out using a liquid crystal as the stationary phase [8–13]. GLC has also been used for many years for studying solute vapors in liquid crystals and liquid crystalline polymers [14–24]. The possibility of using GLC to investigate thermodynamic properties of solutions can provide information on solute–liquid crystal interactions, on which the separation of mixtures is based. In an earlier study Huang et al. [25] showed that the transfer free energy of solutes between two phases of a liquid crystal is nearly constant, in agreement with Flory's theory of liquid crystals. The deviation from the constant was small and found to be a function of solubility parameter rather than the molar volume of solutes. This indicated that the interaction between solute and liquid crystal molecules still plays a role in solution thermodynamic properties.

In many GLC studies the excess free energies of solution, measured at different temperatures, were used to calculate excess enthalpy and excess entropy of solution. Plots of enthalpy vs.

entropy were used in discussions of solution thermodynamics with GLC [26–29]. Linear relationships between enthalpy and entropy of a physicochemical process frequently were found and cited as enthalpy–entropy compensation effects, extrathermodynamic phenomena, or isokinetic relationships. They were found for a variety of thermodynamic and kinetic processes [30–34]. Despite their utility, these relationships also have led to some misunderstanding and controversy. In essence, enthalpy–entropy compensation refers to the experimental observation of a linear relationship between enthalpy (ΔH) and entropy (ΔS) for related processes. The enthalpy–entropy compensation effect can be represented in the following form:

$$\Delta H = \beta \Delta S + \alpha \tag{1}$$

The parameter β, positive with temperature units, is designated the "compensation" temperature. A positive β indicates that when there is a positive variation in enthalpy for a series of solutes, there is an increase in the entropy which compensates for some of the change. The result is a smaller change in ΔG relative to ΔH among different samples. Experimental results of ΔH and ΔS obtained from free energies for a series of temperatures have been used frequently for the plots. However, Krug et al. [35] demonstrated that when enthalpy is calculated using the temperature dependence of free energies, propagated errors often give a straight line with a slope equal to the average temperature of the experimental measurements. Therefore, statistical errors tend to bias the extra-thermodynamic relationship unless the slope of the enthalpy–entropy plot happens to be different from the average of

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the experimental temperatures. Using a general statistical mechanical model, Sharp [36] also showed that a correlation can occur with a slope within 20% of the experimental temperature. This behavior was insensitive to the model details, thus revealing little extra-thermodynamic or causal information about the system.

2. Gas chromatography theory

When an infinitesimal amount of solute sample is introduced into a GLC column with a non-volatile isotropic stationary phase, the specific retention volume of the solute at the column temperature, V_g^T, can be related to the Flory–Huggins interaction parameter, χ, by [1–3,27]:

$$\chi = \ln \frac{RT\nu_1}{P_2^0 V_g^T V_2^0} - 1 + \frac{1}{m} - \frac{P_2^0}{RT}(B_{22} - V_2^0) \qquad (2)$$

where m is the molar volume ratio between the solvent and solute, ν_1 is the specific volume of the stationary phase, and P_2^0, V_2^0, and B_{22} are the vapor pressure, liquid molar volume, and second virial coefficient of the solute, respectively. In the original Flory–Huggins treatment, the interaction parameter, χ, was a constant contact energy difference between solute–solvent interaction and those of the pure components [37]. However, experience has shown that χ usually depends on temperature [38,39]. Guggenheim [39] suggested that χ, the size corrected reduced free energy of solution, be separated so that:

$$\chi = \chi_{H,re} + \chi_{S,re} \qquad (3)$$

where the reduced residual enthalpy of solution, $\chi_{H,re}$, and reduced residual entropy of solution, $\chi_{S,re}$, are defined as:

$$\chi_{H,re} = -T \left(\frac{\partial \chi}{\partial T} \right) = \frac{\Delta \bar{H}_{re}^\infty}{RT} \qquad (4)$$

$$\chi_{S,re} = \frac{\partial (T\chi)}{\partial T} = \frac{-\Delta \bar{S}_{re}^\infty}{R} \qquad (5)$$

The subscript "re" was used to indicate that the quantity was for residual solution properties, in order to distinguish them from the transfer property to be discussed later. Here $\Delta \bar{S}_{re}^\infty$ is the residual entropy of solution or the noncombinatorial part of the entropy of solution. It is associated with solute–solvent interaction. The residual enthalpy of solution is generally considered to be the excess enthalpy of solution. It was noted earlier [26] that the size correction gives a contribution to the entropy of solution but there is no counterpart in the enthalpy of solution. Therefore, in making an enthalpy–entropy plot of solution properties, the size corrected result should be used. The plot of $\chi_{S,re}$ vs. $\chi_{H,re}$ is equivalent to the plot of ΔS vs. ΔH. The slope reaches minus unity when the entropy term has a nearly complete compensation effect. In the earlier study, Huang et al. [27] showed that the plot of $\chi_{S,re}$ vs. $\chi_{H,re}$ was linear for solutes in nonpolar squalane and polar low molecular weight poly(ethylene oxide) (PEO). The slope was about −0.5 and was statistically different from minus unity.

3. Discussion

3.1. Enthalpy–entropy compensation in liquid crystal solvents

As an example, Fig. 1 shows the plot of $\chi_{S,re}$ vs. $\chi_{H,re}$ of solution for twenty-two solutes in 4,4-bis(heptyloxy)azoxybenzene (BHOAB) at the phase transition temperatures. The procedure of measurement was reported previously [16]. The following conclusions can be drawn from Fig. 1 and other systems exhibiting similar behaviors [16–20]:
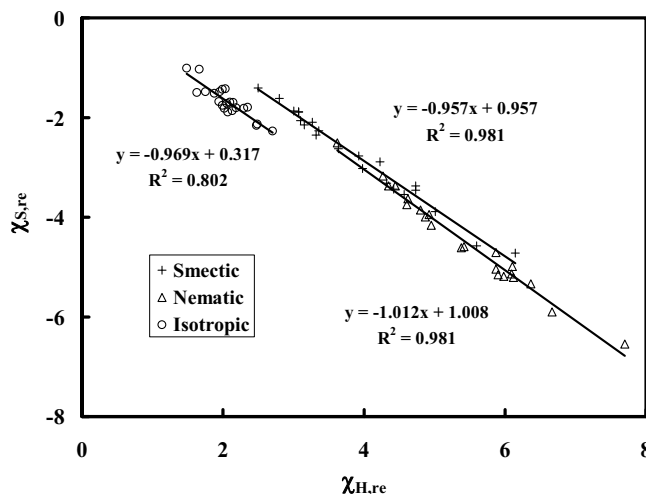

Fig. 1. Plot of reduced residual entropy of solution ($\chi_{S,re}$) vs. residual excess enthalpy of solution ($\chi_{H,re}$) of twenty two solutes in BHOAB. Temperature used in calculation: Smectic phase: 93.7 °C; nematic phase: 123.3 °C; Isotropic phase 123.3 °C.

(A) The first was that in mesophases the enthalpy and entropy of solutions were positive, and the magnitude was higher than for those of isotropic phases. In isotropic phases the range of $\chi_{H,re}$ was from one to three, while the value of the nematic phase reached near eight. In the previous study [26] the range of $\chi_{H,re}$ was about four for a variety of polar and nonpolar solutes in squalane and PEO. The value of $\chi_{H,re}$ for the mesophase was considerably higher than that of the isotropic liquids. The magnitude was about two to three times higher.

(B) The second was that the range of $\chi_{H,re}$ was generally highest for the highest temperature mesophase below the isotropic phase, which was a nematic phase for BHOAB. The phase with the widest $\chi_{H,re}$ range did not necessarily occur at the lowest temperature phase, e.g., smectic phase for BHOAB.

(C) Third, the enthalpy–entropy correlation appeared to be strong compared to the isotropic GLC stationary phases [27] although some scattering still occurred. The scattering was higher for the isotropic phase. Furthermore, the slope of the enthalpy–entropy plot was near minus unity. This showed a higher compensation than the results of isotropic stationary phases [27]. Because the slope was near minus unity, according to the previous argument this correlation alone might not uniquely define a model. A solution model would have to be developed and confirmed separately.

An even more remarkable result occurred when the transfer properties between the two phases of a liquid crystal were compared. Fig. 2 plots the reduced transfer enthalpy, $\chi_{H,tr}$, and reduced transfer entropy, $\chi_{S,tr}$, between different phases of BHOAB at transition temperatures. The transfer properties were calculated from the difference of residual solution properties in two phases. It can be seen that even better correlations existed in the transfer properties. They existed between the two mesophases as well as between a mesophase and the isotropic phase. The transfer enthalpy from smectic to nematic phases was positive, with a magnitude smaller than that of nematic–isotropic phase transfer, which was negative. This was because the nematic phase had a higher enthalpy of solution than the smectic phase, making the transfer from the smectic phase to nematic phase an exothermic process.

Fig. 3 shows the same plot for cholesteryl myristate (CM) [17]. Similar results were obtained. The transfer between smectic and cholestric phases has positive enthalpy, while the transfer between cholestric and isotropic phases has a negative value with higher