TEMPERATURE DEPENDENCE OF THE SOLUTION BEHAVIOUR OF NEMATIC MESOPHASES

H.-J. MOEGEL, G. KRAUS* and M. NOVAK

Martin-Luther-University, Department of Chemistry, 4020 Halle/Saale (G.D.R.)

(First received January 13th, 1984; revised manuscript received January 8th, 1985)

SUMMARY

The temperature dependence of retention volume is analysed for solutions of isomeric dichlorobenzenes and xylenes in a nematic phase. It is shown that deviations of experimental data from a linear relationship between the logarithm of the retention volume, $\ln V_g^0$, and the reciprocal of the absolute temperature, $1/T$, arise from the neglect of the temperature dependence of the enthalpy of solution. Therefore the heat capacities at infinite dilution can be determined by gas–liquid chromatography.

INTRODUCTION

Gas–liquid chromatography (GLC) is a suitable method to determine some thermodynamic properties of non-mesogenic substances at infinite dilution in liquid crystalline solvents. The temperature dependence of the corrected retention volume, V_g^0, permits calculation of the solution enthalpy at infinite dilution, $\Delta_s H_2^\infty$, according to the equation:

$$\left(\frac{\partial \ln V_g^0}{\partial T} \right)_P = \frac{\Delta_s H_2^\infty}{RT^2} \tag{1}$$

To simplify the symbols, in the following we shall omit the indices 2, designating the solute, and ∞, designating infinite dilution.

IR spectroscopic and calorimetric measurements together with simple statistical thermodynamic models can complete the interpretation of GLC data. A linear relationship between the logarithm of the retention volume and the reciprocal temperature is generally held to be approximately valid[1,2]

$$\ln V_g^0 \sim 1/T \tag{2}$$

However, investigations of the solutions of many substances in nematic liquid crystals have shown deviations from such linear correlations[3,4], especially for liquid crystals with long alkyl side chains. In such cases the calculation of the differential molar

enthalpy of sorption at infinite dilution was carried out on the basis of eqn. 2 but assuming that the nematic temperature range can be divided into two subranges, within each of which the experimental data are situated on a straight line. Therefore, besides pretransition effects, two separate temperature ranges associated with different solution properties seem to exist within a single nematic solvent phase. However, we now show that, by reanalysing the corresponding data on the basis of a more precise thermodynamic interpretation, the reason for the appearance of two nematic ranges is the neglect of the temperature dependence of $\Delta_s H$ in eqn. 1.

EXPERIMENTAL

GLC was carried out with a modified Chromatron 18.3 instrument, equipped with a flame ionization detector. A glass capillary column, 27 m × 0.3 mm I.D., deactivated with epoxide resin and coated with 4-*n*-pentyl-acetophenone (O-4-*n*-octyloxybenzoyloxime) (I)

I
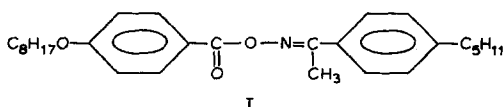
was used. Argon was used as carrier gas. Measurements were made at temperatures between 50 and 120°C. The column temperature was measured by an iron–constantin thermocouple with an accuracy of ±0.2°C.

RESULTS AND DISCUSSION

For thermodynamic analysis, the retention volumes of solutions of *o*-, *m*- and *p*-xylenes and *o*-, *m*- and *p*-dichlorobenzenes in phase I were used as a function of temperature. According to the usual thermodynamic treatment[5–8] taking into account different accuracies of the temperature dependence of $\Delta_s H$, one obtains the relationships 3–5. Neglecting the temperature dependence of the differential molar enthalpy of sorption at infinite dilution in eqn. 1, by integration we obtain the proportionality. This is equivalent to the constancy of the heat capacity, $\Delta_s C_p$, of the solute for the process of dissolution in a nematic phase. In the following it is called the "zeroth" approximation:

$$\Delta_s H^{(0)} = \text{constant}, \quad \Delta_s C_p = 0 \tag{3a}$$

$$\ln V_g^0 = -\frac{\Delta_s H_0}{R} \cdot \frac{1}{T} + a_0 \tag{3b}$$

Taking into account the dependence of $\Delta_s H$ on temperature, to a "first" approximation we have the expressions:

$$\Delta_s H^{(1)} = \Delta_s H_0 + \Delta_s C_p \cdot T, \quad \Delta_s C_p = \text{constant} \tag{4a}$$

$$\ln V_g^0 = - \frac{\Delta_s H_0}{RT} + \frac{\Delta_s C_p}{R} \cdot \ln T + a_1 \tag{4b}$$

In this approximation the heat capacity of the solute in gaseous phase differs from that in solution, but the value of this difference is independent of temperature.

In a "second" approximation the effect of the dependence of $\Delta_s C_p$ on temperature is considered. This leads to the following equations:

$$\Delta_s C_p^{(2)} = \Delta_s C_{p0} + \Delta_s C_{p1} \cdot T \tag{5a}$$

$$\Delta_s H_T^{(2)} = \Delta_s H_{T_1} - \Delta_s C_{p0} \cdot T_1 - \frac{1}{2} \Delta_s C_{p1} \cdot T_1^2 +$$

$$\Delta_s C_{p0} \cdot T + \frac{1}{2} \Delta_s C_{p1} \cdot T^2 \tag{5b}$$

$$\ln V_g^0 = -\frac{1}{R} \left(\Delta_s H_{T_1} - \Delta_s C_{p0} \cdot T_1 - \frac{1}{2} \Delta_s C_{p1} \cdot T_1^2 \right) \frac{1}{T} +$$

$$\frac{\Delta_s C_{p0}}{R} \cdot \ln T + \frac{1}{2R} \cdot \Delta_s C_{p1} \cdot T + a_2 \tag{5c}$$

In eqns. 3–5 the superscript in parentheses indicates the "degree" of approximation, a_0, a_1, a_2, $\Delta_s H_0$, $\Delta_s C_{p0}$ and $\Delta_s C_{p1}$ are constants independent of the temperature, and T_1 represents a fixed temperature within the investigated range. For a better comparison of the results obtained with different approximations, an averaged temperature, $T_1 = \overline{T} = \frac{1}{N} \cdot \sum_{i=1}^{N} T_i$ (N is the number of experimental points), was chosen. Using the method of least squares the constants in eqns. 3b, 4b and 5b were calculated from retention volumes for solutions of isomeric xylenes and dichlorobenzenes in phase I, measured as a function of temperature (see Table I).The trends in the values of the differences in heat capacity for the isomers are not the same as for values of the differential molar enthalpy of sorption. It is evident from the values in Table II that the temperature dependence of the differential molar enthalpy of sorption must be taken into account, whereas the temperature effect on $\Delta_s C_p$ can be neglected. The wider the investigated temperature interval, the larger is the relative error in the use of eqn. 3. The per cent changes in the differential molar enthalpy of sorption, $\Delta_s H$, at infinite dilution for temperature intervals $\Delta T = 1°K$ are reported in Table II. They correspond to twice the systematic errors in $\Delta_s H$ per 1°K, caused by the mentioned neglect of $\Delta_s C_p$. The third column of Table II illustrates that the deviations of experimental points from the least-squares fitted curve may be reduced significantly by use of the first approximation rather than the zeroth one. However, application of the second approximation does not improve further the quality of the fitted curve.

Therefore it is not necessary to divide the temperature range into small parts and to investigate them separately. The solution behaviour within one phase changes

TABLE I

DIFFERENTIAL MOLAR ENTHALPIES OF SORPTION, $\Delta_s H$, AND $\Delta_s C_p$ VALUES FOR DISSOLUTION OF XYLENES AND DICHLOROBENZENES IN NEMATIC PHASE I

Parameter	Dichlorobenzenes			Xylenes		
	o-*	m-	p-	o-	m-	p-
$\Delta_s H^{(0)}$ (kJ mol^{-1})	−40.8	− 37.36	− 37.58	− 32.84	− 32.19	− 33.24
$\Delta_s H_0^{(1)}$ (kJ mol^{-1})	—	− 153.68	− 158.86	−137.15	−102.90	− 88.34
$\Delta_s C_p^{(1)}$ (J K^{-1} mol^{-1})	—	−337.9	−352.4	304.0	206.1	160.1
$\Delta_s H_0^{(2)}$ (kJ mol^{-1})	—	−325.94	−392.06	− 130.03	− 63.76	− 67.49
$\Delta_s C_{p0}^{(2)}$ (J K^{-1} mol^{-1})	—	1338	1707	263	−2	39
$\Delta_s C_{p1}^{(2)}$ (J K^{-2} mol^{-1})	—	−2.90	−3.94	0.12	0.66	0.35

* Where values are not given, the scattering in the experimental points ($V_{g,i}$, T_i) is too large, preventing application of the first and second approximations.

continuously as a smooth function of temperature. Mixtures of the nematic phase I or the corresponding 4′-heptyloxy derivative with small concentrations of 2-octanol were investigated by IR spectroscopic measurements of the temperature dependence of the frequency shift of the OH-band, in order to detect the existence of two nematic ranges[9]. However, the scattering of the measured values on the temperature axis is too large to enable a definite conclusion to be drawn, i.e. to distinguish between a non-linear curve and two lines.

TABLE II

TEMPERATURE EFFECT ON THE DIFFERENTIAL MOLAR ENTHALPY OF SORPTION, $\Delta_s H$, AND ON $\Delta_s C_p$ AND THE QUALITY OF THE FITTED CURVE FOR THE RETENTION VOLUMES FOR DISSOLUTION OF o-, m- AND p-XYLENES AND m- AND p-DICHLOROBENZENES IN NEMATIC PHASE I

Compound	Change in $\Delta_s H^{(1)}$ for $\Delta T = 1°K$ (%)	Change in $\Delta_s C_p^{(2)}$ for $\Delta T = 1°K$ (%)	Deviation of retention volume* (%)		
			$V_g^{0(0)}$	$V_g^{0(1)}$	$V_g^{0(2)}$
o-Xylene	1	0.1	1	0.6	0.6
m-Xylene	0.5	0.2	0.7	0.5	0.5
p-Xylene	0.5	0.3	0.6	0.4	0.4
m-Dichlorobenzene	1	1	0.7	0.3	0.3
p-Dichlorobenzene	1	1	0.8	0.3	0.3

* Calculated from

$$V_g^{0(k)} = \frac{1}{N} \cdot \sum_{i=1}^{N} \left(1 - \frac{V_{g,th,i}^{0(k)}}{V_{g,exp,i}^0}\right) \cdot 100\%$$

where $k = 0, 1, 2$ correspond to the zeroth, first and second approximations.

The application of the above approximations (a) gives a complete quantitative description of the temperature dependence of the retention volumes in the nematic phase outside the pretransition range and (b) allows a determination of the change in heat capacity of non-mesogenic substances at infinite dilution in liquid crystalline solvents. The $\Delta_s C_p$ values can be correlated with statistical thermodynamic estimation of the rotational and vibrational degrees of freedom and of the change in translational energy of the solute molecules[10]. However, given the present precision of measurements it is impossible to determine the correct dependence of $\Delta_s C_p$ on temperature.

CONCLUSIONS

The differential molar enthalpy of sorption of non-mesogenic compounds at infinite dilution in some nematic solvents depends on the temperature within the nematic range when liquid crystals with long alkyl side chains are used. By means of GLC it is possible to determine the $\Delta_s C_p$ values for dissolution of non-mesogenic substances in a nematic solvent.

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