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GAS CHROMATOGRAPHY WITH ANISOTROPIC LIQUIDS

PARTITION COEFFICIENTS AT THE MESOPHASE–ISOTROPIC PHASE TRANSITION POINT

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SUMMARY

Liquid crystals ("mesophases") of different molecular weight and different molecular constitution show a common and typical solute–solvent interaction behaviour, especially in the vicinity of their phase transition temperature θ_i, the "clearing point". If for a certain solute specific retention volumes V_g in different (i) solvents are plotted logarithmically against the reciprocal transition temperature, log $V_g^{(i)}$ varies linearly with $1/\theta_i$ for very different mesomorphic systems. Correspondingly the limiting activity coefficients f_i^∞, when plotted in the same way, also give a linear relationship In f_i^∞ *versus* $1/\theta_i$, which is interpreted as a "corresponding state behaviour". This linear relationship transforms into a universal linear function if the activity coefficients are calculated on a mass base and not —as is usually done— on a molar base. The interesting fact is that such a behaviour has also been observed with polymer systems, as described by Roberts and Hawkes. The reasons are discussed.

In the last 12 years, considerable experience has been gained with liquid crystalline stationary phases, and a large number of volatile substances (predominately isomers) have been separated using liquid crystals as stationary solvents in gas–liquid chromatography (GLC). The theoretical background has been given in the literature[1-6]. In this paper are discussed the results obtained during practical work with mesophase GLC systems[5] but not yet interpreted in a general way. It is shown that mesophases with very different chemical structures form typical solvent systems that show interactions parallel to certain high-molecular-weight solvents, and that lead to the surprising result that mesomorphic solvents, when they approach the transition point into the isotropic phase, act in such a homogenous way that one can deduce from experimental data (activity coefficients, properly defined) a "corresponding state" behaviour for the different liquid crystalline solvents.

The corresponding state condition, which is well known to occur at the critical point of a liquid or, to a lesser extent, at its normal boiling point, states that molecular interactions are reached that equal one another with respect to their stability in a certain state of aggregation. We shall not discuss the interesting question of whether or not "critical melting" of organic substances does occur, but it can easily be realized

that, in general, the stationary phases used in chromatography at temperatures far
.removed from their characteristic transition points (melting, transformation between
polymorphous modifications) cannot be regarded as being in a corresponding state.
Further, it is well known that even the melting point does not serve very well as a
"corresponding state" temperature because of the complicated lattice-dependent
parameters, dependent on which polymorphous modifications and how many of
them have taken place during the thermal history of the phase. It was therefore hoped
that the transition point of a mesophase into the coexisting isotropic phase, a transi-
tion that is "weakly first order" and whose molar entropy of transformation shows
interesting regularities, would be such a "corresponding state condition". We looked
at solubility effects, which are related in a regular manner to such a special state of
order. Consider, for better understanding, the "excess free energy" of an anisotropic
solution process with respect to the isotropic process: the transformation into the
highly ordered, denser anisotropic phase can be understood by the well known rela-
tionship

$$\frac{RT \, \partial \ln f}{\partial P} = V_2 - V_2^{\infty} \tag{1}$$

where f is the activity coefficient, V_2 is the partial molar volume of the solute and V_2^{∞}
its partial molar volume at infinite dilution. Because each mesophase being formed
from the isotropic phase is followed not only by a higher degree of order, but also
by a compression of the system, the activity of the solute must be enhanced. We can
now examine such an anisotropic solvent–solute system a few degrees below the trans-
formation point into the isotropic phase. The solute is kept constant, and its constitu-
tion should be chosen in such a way that the solute–solvent interaction properties are
predominately the same as those between the solvent molecules themselves, i.e., dis-
persion forces related to geometrical features. We therefore chose o-xylene as the
"indicator solute". As found elsewhere[7], a surprising linear interdependence between
ln V_g^N (specific retention volume) and the reciprocal of the above temperature θ, the
"clearing point", results. This type of regularity can now be understood if it is re-
membered that, as far as the specific retention volume is concerned, we operate with
a magnitude (V_g^N) that is not defined on a molar base, because mass is used as the
unit for the calculation and definition of molar free energy (V_g^N, K or f_2^{∞}) which means
principally the same. (K is the partitition coefficient.)

The solution is as follows. We define the limiting activity coefficient, f_2^{∞}, not
on a molar but on a mass unit basis. Starting with the Raoult–Henry law, we have

$$p_2 = p_2^0 \cdot f_2^{\infty} \cdot x_2 \approx p_2^0 \cdot f_2^{\infty} \cdot \frac{m_2/M_2}{m_1/M_1} \tag{2}$$

where p_2^0 is the vapour pressure of the pure solute. Introducing

$$_w f_2^{\infty} \equiv f_2^{\infty} \cdot \frac{M_1}{M_2} \tag{3}$$

it follows that

$$p_2 = {_w f_2^{\infty}} \cdot p_2^0 \cdot \frac{m_2}{m_1} \tag{4}$$

If the same solute is always considered, we can delete M_2 and it is evident that the newly defined term $_wf_2^\infty$ is related in the well known way to the specific retention volume with the only difference that the magnitude M_1 is not needed explicitly:

$$_wf_2^\infty \equiv \frac{273\,R}{V_g^N \cdot p_2^0}$$

(5)

Using the defined activity coefficients as calculated from V_g^N given above, one obtains a nearly straight line, relating $\ln\,_wf_2^\infty$ to $1/0$, where 0 is the clearing temperature. If one had used the f_2^∞ values on a molar basis, the relationship would not show such a regular "corresponding state" behaviour.

In fair correspondence with the solubility of homologous series of polymers[5], the reason for this dependence can easily be seen. It is certain that a predominating dispersion force interaction, as it exists between the mesogenic molecules themselves, determines in the same way the activity of the solute molecules, at least as far as their polarizability-dependent part is concerned. Thus it can be understand that the o-xylene interacts with the solvent molecules by a space-dependent rather than a number-dependent mechanism. Such an interaction has also been shown recently to act in the case of polymer homologues, where the situation is similar and has been discussed briefly by Roberts and Hawkes[8].
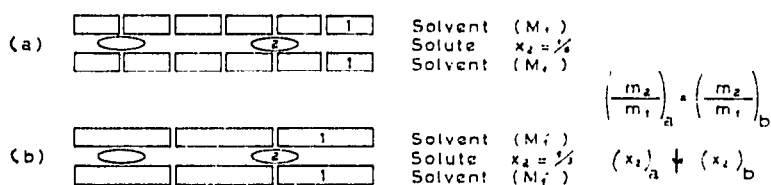

Fig. 1. Diagram showing that the solute–solvent interaction depends on the mass (or volume) ratio rather than on the molar (i.e., number) ratio.

Let us assume that the two systems a and b in Fig. 1 have the same solute activity. Assuming further that this activity depends on the probability of moieties 1 and 2 contacting one another, it can easily be understood that it will not depend on the number ratio but on the ratio of contacting sites being equal in both instances and independent of the number of individual solvent molecules. Starting with the experimental results, we have the general function

$$\ln f_2^\infty \cdot M_1 = \frac{A}{T} + C$$

(6)

Introducing M_2, the "molar weight" of the solute, which is always the same in the following calculations, we obtain

$$\ln f_2^\infty \cdot \frac{M_1}{M_2} \equiv \ln\,_wf_2^\infty = \frac{A}{T} + C'$$

(7)

From this we derive, introducing the excess potential μ^E

$$\ln f_2^\infty \cdot \frac{M_1}{M_2} = \frac{\mu^E}{RT} + \ln\left(\frac{M_1}{M_2}\right)$$

(8)

and with $\mu^E = h - Ts^E$ it follows that

$$\ln {}_wf_2^\infty = \frac{h}{RT} - \frac{s^E}{R} + \ln \left(\frac{M_1}{M_2}\right) \tag{9}$$

To a first approximation, the sum of the last two terms is constant, even with a large variance of M_1. Hence s^E depends strongly on the molecular weight ratio M_1/M_2 or, if M_2 is kept constant during the experiment, on M_1:

$$s^E = R \ln \left(\frac{M_1}{M_2}\right) + C^{11} \tag{10}$$

Of course, both enthalpy and entropy are temperature-dependent functions, but this dependence is relatively small, and it can be stated that the general and uniform behaviour has led to a special expression for the excess entropy, s^E being defined in its original sense, i.e., on a molar basis.

The ratio of molecular weights enters explicitly, and the value of the constant C is obtainable by experiment. C can also be regarded as characteristic for mesophases. In the same way as previously, one could define a new μ^E on a mass fraction basis:

$$RT \ln {}_wf_2^\infty = {}_w\mu^E \tag{11}$$

Hence one obtains

$$_w\mu^E = h - T\left[s^E - R \ln \left(\frac{M_1}{M_2}\right)\right] \tag{12}$$

with

$$s^E - R \ln \frac{M_1}{M_2} = {}_ws^E \tag{13}$$

A consequence of the newly defined activity coefficient, ${}_wf_2$, is that if the specific retention volume of a solute is measured just below the clearing point of the mesomorphic phase, we obtain a straight line if $\ln V_g^N$ is plotted against $1/\theta$. To a good approximation, the same linear dependence also holds for the partition coefficients, K, because $K = V_g^T \cdot \varrho$, where ϱ is the density of the stationary phase.

The explanation is simple. Consider a fixed solute (2):

$$V_g^N (j) = \frac{273\,R}{p_2^0 \cdot M_j \cdot f_2^\infty} \tag{14}$$

("2" kept constant, M_j changing) and

$$\ln V_g^N(j) = -\ln p_2^0 - \ln M_j f_2^\infty + \ln 273R = \left[\frac{-\Delta H^v}{T} + \text{constant}\right] - $$

$$\left[\frac{A}{T} + \text{constant}'\right] + \text{constant}'' \tag{15}$$

The first term is independent of the solvent, and the second term is, to a first approximation, a universal function of temperature. Hence the linear eqn. 16 reflects the same as eqn. 6:

$$V_g^N (j) = \frac{-\Delta H^v - A}{T} + \text{constant}^{\text{III}}$$ (16)

In this equation, T naturally can be chosen as θ_j, where θ_j is the clearing temperature of any nematic melt.

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