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CHROMATOGRAPHIC METHOD FOR DETERMINING THE PHYSICO-CHEMICAL AND THERMODYNAMIC CHARACTERISTICS OF COLLOIDAL SYSTEMS

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SUMMARY

The physico-chemical and performance characteristics of lubricant-type colloidal systems depend to a great extent on their aggregative state. Thermodynamic sorption parameters, determined by means of reversed-phase chromatography, are proposed for assessing the aggregative state of colloidal systems. It is shown that the retention characteristics and thermodynamic parameters of sorption may serve as a measure of interphase and surface tension, which predetermine the free surface energy of heterogeneous systems.

INTRODUCTION

When choosing the most efficient method for using chromatographic information in the assessment of lubricant physico-chemical and performance characteristics, the following equation is proposed:

$$A = \varphi \left(\sum_{x=i}^{x=n} a_i x_i + \sum_{x'=1}^{x'=n} a_i' x_i' + \ldots + \sum_{x^n=1}^{x^n=n} a_i^n x_i^n \right) \tag{1}$$

where A = system characteristic; a_i = a component or a group of composition component property; x_i = a component or a composition component group concentration in the composition constituent; φ = coefficient characterizing the degree of composition component interaction. The degree of composition component interaction is calculated from the free surface energy.

Several methods have been developed for the direct determination of the free surface energy of heterogeneous colloidal systems[1-3]. However, despite various improvements, the errors in the experimental determination of the surface layer thickness remain pronounced, leading to inaccurate results.

We propose to evaluate the free surface energy with the help of retention characteristics and thermodynamic parameters of sorption, determined by means of reversed-phase chromatography. Then the Gibbs equation[4] acquires the following form:

$$\Delta G = \Delta G_{1(S)} + \Delta G_{2(S)} + \Delta G_i \qquad (2)$$

where ΔG = the system free energy; $\Delta G_{1(S)}, \Delta G_{2(S)}$ = free energy of sorption of volumetric phases; ΔG_i = composition component interaction energy.

EXPERIMENTAL

The studies were carried out on a gas chromatograph with a heat conductivity detector under the following conditions: column, 0.49 m × 0.35 cm I.D.; evaporator temperature, 150°C; column temperature, 50°C; carrier gas flow-rate, 20 ml/min; sample volume, 0.2 μl; analysis duration, 1–2 min; standard, n-hexane. The column was packed with a mechanical mixture of Inertone AW and a lubricant (0.3 g). The specific retention volume of the standard was calculated based on the experimental retention value with regard to the mass of the sample being analysed. The relative standard deviation was less than ±0.05 of the value measured.

The compositions studied contained 5–20% of a thickening agent (soaps, pigments, silica gels, additives) and a liquid base (oils, hydraulic fluids). A sample of the standard compound was fed into the column, charged with the sorbent; the the sorbate yield with time was noted, based on the peak maximum, and the specific retention volume (V_g) was determined. Values of thermodynamic parameters[5] were calculated on the basis of V_g.

RESULTS AND DISCUSSION

Fig. 1. shows the relationship between $\Delta G_{(S)}$ for n-hexane and the colloidal system composition. It was assumed that the model system (mineral instrument oil, soap) was a mechanical mixture, that there was no interaction between the dispersion phase and the dispersion medium ($\Delta G_i = 0$). However, in real systems a deviation of ΔG_i resulting from interaction of the components of the the mixture is observed.

We can demonstrate the viability of using sorption thermodynamic parameters to assess the thermodynamic state of the system. Colloidal systems are characterized by two major features: heterogeneity and dispersivity. Heterogeneity means that there is surface tension (σ) and dispersivity is determined by the interphase (S). Retention volume is proposed for interphase assessment. It can be shown that the retention volume is an actual measure of the dispersivity of the system. Let us take a non-polar compound as a sorbate, e.g., n-hexane; the intermolecular interaction between n-hexane and the stationary phase will then be characterized only by the dispersive interaction, which is expressed by the equation[4]

$$u_{ads} = \pi cn/6x^3 \qquad (3)$$

where u_{ads} = interaction energy; c = constant; n = number of molecules (atoms) per unit volume of adsorbent; x = distance between the adsorbed atom or the molecule and the adsorbent surface. When it is considered that the size of the sorbate molecule remains constant, then a change in the size of the sorbent molecule must result in a change in the retention volume of the sorbate, namely that particle aggregation brings about a decrease in V_g and an increase in dispersion.
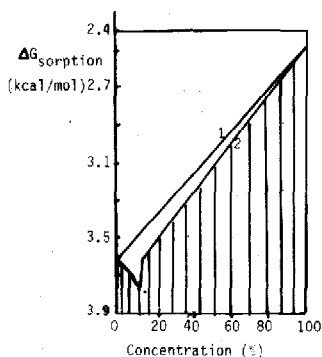
Fig. 1. Relationship between sorption free energy of *n*-hexane and the colloidal system composition. 1, Theoretical curve; 2, actual curve.

As an example, Fig. 2 shows the relationship between log V_g for *n*-hexane and the temperature in the stationary phase (residual oil). Residual oil (a lyophilic colloidal system) changes its aggregative state under the influence of temperature in the range 60–90°C. Judging by the change in value, there is system aggregation at 60°C, but it disperses at 90°C. This is confirmed by other analytical methods[6]. The fact that there has been attained proportional retention volume of the system dispersivity degree can be considered not only in terms of molecular interactions but also in terms of interphase formation. Let us consider this approach with the example of two greases, one of which is a lyophilic colloidal system (mineral oil thickened by lithium stearate) and the other is a lyophobic system (a fluorinated ester thickened by a pigment). The relationship between the change in retention volume and the component concentration for the first system is shown in Fig. 3 (curve 1) and for the second system in Fig. 3 (curve 2). It is obvious that the retention volume of the lyophilic system increases with increase in the dispersion phase concentration and reaches a maximum at an oil to thickener ratio of 12:88. A further increase in dispersion phase
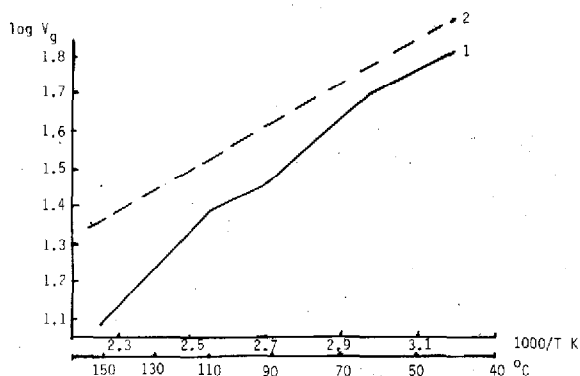

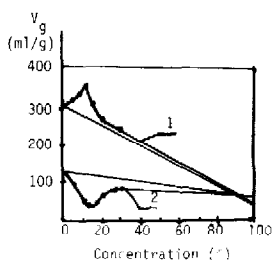Fig. 2. Relationship between log V_g of *n*-hexane and temperature. 1, Squalane; 2, residual oil.

Fig. 3. Relationship between V_g of n-hexane and dispersion phase concentration of colloidal systems. 1, Lyophilic system; 2, lyophobic system.

concentration results in a decrease in sorbate retention volume. With an increase in retention volume the dispersion of the system increases, which results in an interphase increase. However, the interphase increases only to a certain level and reaches a maximum at a thickener to oil ratio of 12:88. A higher thickener volume results in coagulation of litium stearate particles, bringing about an interphase decrease and consequently a reduction in the sorbate retention volume.

Let us now consider the lyophobic system. According to Rebinder[7], the aggregative instability of a lyophobic system increases with reduction in particle size, but their number per unit volume increases. A small increase in retention volume at the beginning of the curve shows the interphase growth; its decrease starts even at a thickener concentration of 4–5% and reaches a minimum at an thickener to oil ratio of 12:88.

The discussed examples permit the conclusion that retention volume may serve as a measure for the assessment of the heterogeneous dispersion system interphase, i.e., it can be used to evaluate the degree of dispersivity of these systems.

The other characteristic that determines the surface energy is surface tension. We can express it by means of the retention parameters. Gibbs equation[7] relates adsorption to surface tension change:

$$\Gamma = \frac{d\sigma}{dc} \cdot \frac{c}{RT} \tag{4}$$

where Γ = adsorption; c = concentration; R = gas constant; T = absolute temperature; σ = surface tension. The term $d\sigma/dc$ in eqn. 4 reflects the influence of the nature of the substance on adsorption. Processes running in the chromatographic mode are characterized by adsorption at low concentrations, which can be described by Henry's equation:

$$\Gamma = K_\Gamma c \tag{5}$$

where K_Γ is Henry's distribution (adsorption, solubility) constant (coefficient).

Kiselev showed that the specific retention volume ($V_g = V_n/m$), where V_n is retention volume and m is stationary phase mass, has the properties of a physicochemical constant, proportional to Henry's coefficient:

$$V_g = \frac{K_\Gamma}{\rho} \tag{6}$$

where ρ is the stationary phase density.

The sorption energy equation

$$\Delta G_S = RT \log K_\Gamma \tag{7}$$

suggests

$$\Delta G_S = RT \log V_g \tag{8}$$

We can determine K_Γ from eqns. 5 and 6:

$$\Gamma = K_\Gamma c = \frac{d\sigma}{dc} \cdot \frac{c}{RT} \tag{9}$$

Thus,

$$K_\Gamma = \pm \frac{1}{RT} \cdot \frac{d\sigma}{dc} \tag{10}$$

$$V_g = -\frac{1}{RT} \cdot \frac{d\sigma}{dc} \cdot \rho \tag{11}$$

Hence the retention volume is inversely proportional to the surface tension. Considering that surface tension is a power characteristic,d we can express it by means of ΔG_S:

$$-\Delta G_S = RT \ln V_g \approx \frac{\rho}{RT} \cdot \frac{d\sigma}{dc} \tag{12}$$

As ρ/RT is constant,

$$\Delta G_S \approx B \cdot \frac{d\sigma}{dc} \tag{13}$$

i.e., surface tension is proportional to the excess surface energy of sorption.

Let us now consider the change in surface tension at the interphase of lyophilic systems 1 and 2. The sorption change in both systems is shown graphically in Fig. 4. It can be seen that as far as the lyophilic system is concerned, the surface tension decreases when the thickener concentration increases, reaching a minimum when the thickener concentration is 12%. At this point the contribution of the surface tension to the total surface energy is at a minimum.

For the lyophobic system, the surface tension increases and is at a maximum (Fig. 4) when the pigment thickener concentration is 12%, i.e., the contribution of the surface tension to the surface energy of the system is maximal. In addition, the surface tension of lyophilic colloidal systems will be lower than the marginal surface tension of the dispersion phase and of the dispersion medium (σ_{m_1}, σ_{m_2}), but it will be higher in lyophobic systems. This is consistent with Rebinder's concepts of lyophilic and lyophobic systems[9].

Hence the excessive free energy of sorption, which is easily determined by chromatography, may serve as a means of assessing the surface tension of colloidal systems and permits their degree of heterogeneity to be determined. It should be mentioned that the σ value is the decisive factor in evaluating the surface energy of both lyophilic and the lyophobic systems; this value determines the sign of the surface energy of the system. The S value also contributes to the surface energy but it is not decisive.

Based on the foregoing discussion, we propose to use a criterion that takes into account the deviation of the surface tension of a real system from the marginal values of the composition components for assessing the aggregative stability of colloidal dispersion systems. This criterion can be determined graphically from (Fig. 5)

$$\varphi = \frac{\sigma}{\sigma_{m_1 m_2}} \qquad (14)$$

where φ is the aggregative stability criterion and $\sigma_{m_1 m_2}$ is the component surface tension.

The σ and $\sigma_{m_1 m_2}$ values are determined on the basis of chromatographic data, $\sigma \approx \Delta G_S$; $\Delta \sigma_{m_1 m_2} = \Delta G_m - \Delta G_S$, for the standard substance in a hypothetical system that has no component interaction. $\Delta \sigma$ characterizes the degree of interaction of the mixture components. For lyophobic systems φ is greater than 1; the greater the deviation from 1, the higher is the aggregative stability of the system. For lyophilic systems, their aggregative stability has φ lower than 1.

A number of methods for determining the physico-chemical and performance characteristics of lubricants have been developed based on the use of this aggregative stability criterion of colloidal systems, e.g., determination of the thermodynamic compatibility of lubricant components[10], determination of the vapour pressure in oils and greases[11] and the assessment of structural transformations in oils and additives, depending on the concentration and nature of the additives and also on the engine operating conditions[6].
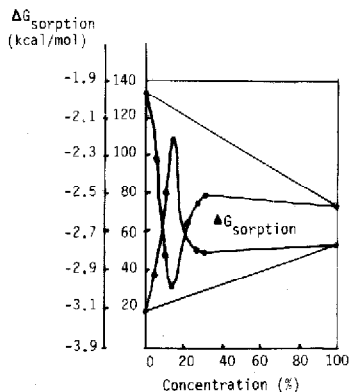

Fig. 4. Relationship between $\Delta G_S(\sigma)$ and composition component concentration of lyophilic and lyophobic systems.
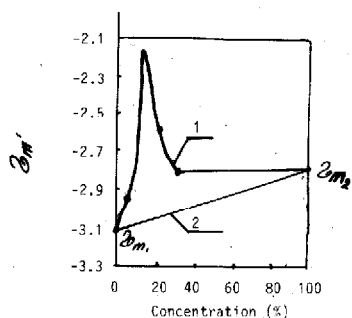
Fig. 5. Graphical method for determining aggregative stability criterion of lyophobic colloidal systems. Curve 2, Hypothetical system; curve 1, actual system.

CONCLUSIONS

A method of assessing the aggregative stability of colloidal systems is proposed, based on determining the free surface energy of the system. It has been shown that the retention characteristics and thermodynamic parameters of sorption can be used to determine the surface energy components (surface tension, interphase). Based on the use of the aggregative stability criterion, a number of procedures have been developed for determining the physico-chemical and performance characteristics of lubricants.

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