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Vapor Pressure of a Mixed System of Asphaltene and Organic Solvent

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The vapor pressure of a system in which it is assumed that the maltene component in petroleum asphalt has been replaced by an organic solvent, *i.e.*, a mixed system of an asphaltene component and an organic solvent, was measured over a wide range of composition. The experimental results were then analyzed on the assumption that such a system is a binary system and that the equation $\mu_1=\mu_1^\circ+\boldsymbol{R}T\ln(1-v_2)+(1-1/z)v_2+\chi_1 v_2^2$ which Flory and Huggins derived for the chemical potential of a solvent of a linear, high-polymer solution which is not relatively dilute is applicable; the volumetric ratio, z, of the asphaltene particle and solvent molecule and the value of the parameter, χ_1, of the interaction of the asphaltene and solvent molecules were obtained. The above results made it clear that mixed systems of asphaltene plus chloroform and carbon tetrachloride all form a homogeneous phase over the entire composition range, but in the case of a cyclohexane system, separation into 2 phases occurs in the mixed composition range of 3.0 vol%—40 vol% asphaltene and a dilute phase of 3.0 vol% asphaltene and a concentrated phase of 40.0 vol% coexist. It may be assumed from the above results that there is a possibility of the presence of a state in which separation into 2 phases is also present in the case of asphalt.

The petroleum asphalt is composed of three components, which are called "asphaltene", "asphaltic resin," and "asphaltic oil," and it is generally accepted that it has a colloidal structure in which the asphaltene molecules or the micelles which absorb or adsorp the asphaltic resin disperse in asphaltic oil. However, there has been no study confirming such a colloidal structure of asphalt experimentally.

Here, we measured the vapor pressures of mixtures asphaltene with various organic solvents and examined the dissolved states of the asphaltene in the systems, the sizes of the asphaltene molecules or particles, and the interaction between the asphaltene and the organic solvent molecule. It can be considered that this examination is the first step in elucidating the structure of asphalt, since the above-mentioned system can be regarded as one in which a maltene component which is the mixture of asphaltic oil and resin is replaced by an organic solvent.

Experimental

Materials. Straight asphalt manufactured by the Nippon Sekiyu Co., Ltd., was used as the sample from which the asphaltene component was separated. The values of the penetration degree[1] and the ring and ball softening point[2] of this asphalt were 73 and 49 respectively.

Cyclohexane, benzene, chloroform, and carbon tetrachloride which had been purified according to the common method were used as the solvents to dissolve the asphaltene.

Separation of Asphaltene from Asphalt. The straight asphalt described above was mixed with 3 volumes of *n*-hexane, shaken, and left to stand for a long time; then the supernatant solution of the mixture was removed by decantation. The insoluble component separated from the mixture was mixed again with 3 volumes of *n*-hexane; this mixture was shaken and filtered, and the residue was used as the sample of asphaltene in the experiments.

Method for the Measurement of the Vapor Pressure. A quartz spring, on which a small glass basket containing the

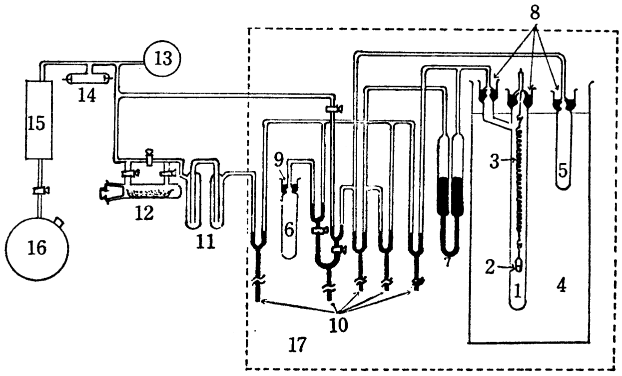

Fig. 1. Apparatus.
1. Glass tube 2. Glass basket 3. Quartz spring balance 4. Liquid thermostat 5, 6. Solvent stock container 7. Mercury manometer 8, 9. Mercury seal 10. Mercury cut 11. Trap 12. Desiccating agent 13. Macleod gauge 14. Geissler tube 15. Mercury diffusion pump 16. Rotary pump 17. Air thermostat

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[1] JIS K 2530.

[2] JIS K 2531.

sample was hung, was placed in a long glass tube which was connected to a mercury manometer and a mercury diffusion pump and placed in a liquid thermostat.

The glass tube was evacuated, and then it was closed by shutting a mercury cut; a solvent vapor was introduced into the tube, and after giving a suitable length of time for the temperature equilibration to be reached, the vapor pressure of the sample mixture was read on the mercury manometer to within 0.001 cm. This apparatus is drawn schematically in Fig. 1. The pressure inside of this vacuum line without a sample, as measured by a Macleod gauge, was 10^{-5} mmHg. The compositions by the volume fractions of the systems were determined by means of the weight of the sample mixture, which was measured by means of the quartz-spring balance, and the densities of the asphaltene and the solvent. The dried asphaltene powder did not show the vapor pressure; accordingly, the asphaltene was treated as a non-volatile material.

Results and Discussion

Many difficulties arose in the theoretical treatment of the experimental results, for the asphaltene is not a single compound, but a mixture of several kinds of compounds; further, our information about these compounds and the molecular forms is sparse. Consequently, we will discuss the experimental results on the basis of two assumptions. The first is that the mixture of the asphaltene and organic solvent is a binary system, and the second is that the equation for a chemical potential of the solvent of a relatively concentrated solution of linear high polymers;

$$\mu_1 = \mu_1^\circ + \boldsymbol{R}T\ln(1-v_2) + \left(1-\frac{1}{z}\right)v_2 + \chi_1 v_2^2 \tag{1}$$

which was derived by Flory[3] and by Huggins[4], can be applied to the system of the asphaltene and an organic solvent. In the above equation, μ_1 and μ_1° are the chemical potentials of the solvent in the system and the pure solvent respectively; z, the ratio of the molar volume of the solute molecule to the solvent molecule; χ_1, the parameter of the interaction between a solute and solvent molecules; v_2, the volume fraction of the solute in the system; $\boldsymbol{R}$, the gas constant, and T, the absolute temperature of the system.

On the other hand, when the vapor is assumed to be an ideal gas, the activity, a_1, of a solvent in the solution of a non-volatile material is given by;

$$a_1 = \frac{p}{p_0} \tag{2}$$

where p and p_0 are the vapor pressures of the solvent over, respectively, a solution and a pure solvent. When the vapor is assumed to be an imperfect gas, a_1 is represented by;

$$a_1 = \frac{p}{p_0}\exp\left[\frac{-B}{\boldsymbol{RT}}(p_0-p)\right] \tag{3}$$

where B is the second virial coefficient of the vapor of a pure solvent at T°K. In Eq. (3), exp $[(-B/\boldsymbol{R}T)(p_0-p)]$ is the factor for the gas-imperfection correction. The relative deviation from 1 of this value is estimated to be 1.5% at most, and about 0.5% in mean value, in relation to the data of this experiment. Here, however, we ignored these gas-imperfection corrections and used Eq. (2), because we could not find the accurate values of B for the vapors at every measuring temperature of every solvents. The chemical potential of the solvent in solution can, therefore, be represented by the following equation:

$$\mu_1 = \mu_1^\circ + \boldsymbol{R}T\ln\frac{p}{p_0} \tag{4}$$

A comparison of Eq. (1) with (4) gives:

$$\ln a_1 = \ln\frac{p}{p_0} = \ln(1-v_2) + \left(1-\frac{1}{z}\right)v_2 + \chi_1 v_2^2$$

or (5)

$$a_1 = \frac{p}{p_0} = (1-v_2)\exp\left[\left(1-\frac{1}{z}\right)v_2 + \chi_1 v_2^2\right]$$

In general, the interaction parameter, χ_1, can be determined by using the observed a_1 and z values, which are evaluated by means of the molecular weight. However, as the molecular weight of asphaltene has not been found, it was necessary to determine the values of both z and χ_1 at the same time, Eq. (5) was, therefore, rewritten as follows:

$$Y = \frac{\ln\frac{p}{p_0} - \ln(1-v_2)}{v_2} = \left(1-\frac{1}{z}\right) + \chi_1 v_2 \tag{6}$$

If neither the z value nor the χ_1 value depends on the volume fraction, the plots of Y *vs.* v_2 should be linear. The intercept and the slope of the straight line will, then, give the values of $(1-1/z)$ and χ_1 respectively.

The plots of Y *vs.* v_2 for the four kinds of systems are shown in Figs. 2—5. As can be seen in these figures, the relation of Y to v_2 was found to be linear; accordingly, the values of χ_1 and z could be determined simultaneously. The values thus obtained for each system are shown in Table 1.

The above results show that χ_1 does not depend on v_2. Furthermore, the plot points of Y *vs.* v_2 at the different equilibrium temperatures were found to be on the same straight line. It may be thought that χ_1 does not depend on the temperature, either. Ac-

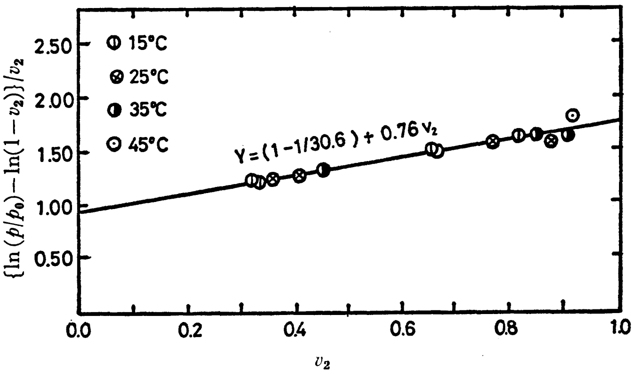

Fig. 2. A plot of $\{\ln(p/p_0)-\ln(1-v_2)\}/v_2$ *versus* volume fraction of asphaltene v_2 for the mixed system of asphaltene and cyclohexane.

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[3] P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).

[4] M. L. Huggins, *ibid.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942).

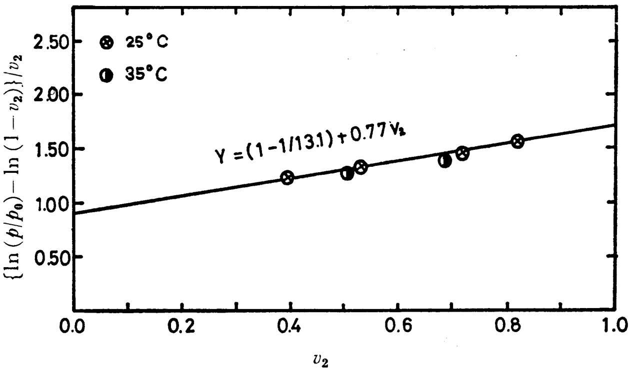

Fig. 3. A plot of $\{\ln(p/p_0)-\ln(1-v_2)\}/v_2$ *versus* volume fraction of asphaltene v_2 for the mixed system of asphaltene and benzene.

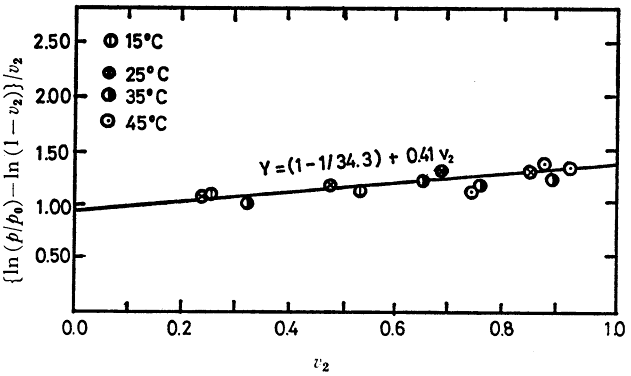

Fig. 4. A plot of $\{\ln(p/p_0)-\ln(1-v_2)\}/v_2$ *versus* volume fraction of asphaltene and chloroform.

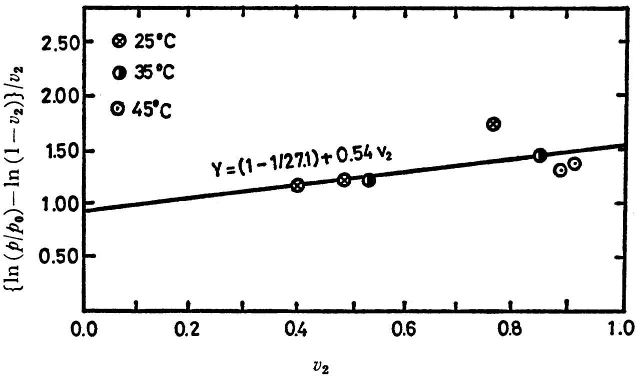

Fig. 5. A plot of $\{\ln(p/p_0)-\ln(1-v_2)\}/v_2$ *versvs* volume fraction of asphaltene v_2 for the mixed system of asphaltene and carbon tetrachloride.

cording to Flory,[3] χ_1 is a dimensionless quantity formally defined by:

$$\chi_1 = \frac{qx_{12}\Delta w_{12}}{kT} \tag{7}$$

where Δw_{12} is the exchange interaction energy per molecule; k, the Boltzmann constant, T, the absolute temperature; q, the coordination number about a lattice in solution and x_{12}, the number of segments in a solvent molecule. The mixing enthalpy change, ΔH_m, is represented by:

$$\Delta H_m = -kT^2\left(\frac{\partial \chi_1}{\partial T}\right)n_1 v_2 \tag{8}$$

Table 1. The volumetric ratio z of solute and solvent molecules, the interaction parameter χ_1 and the critical volume fraction and χ_1 value for phase separation

Solvent	Volumetric ratio	Interaction parameter	Critical values	
			Volume fraction	Interaction parameter
	z	χ_1	$(v_2)_c$	$(\chi_1)_c$
Cyclohexane	30.6	0.76	0.18	0.68
Benzene	13.1	0.77	0.27	0.78
Chloroform	34.3	0.41	0.17	0.67
Carbon tetrachloride	27.1	0.54	0.19	0.69

where n_1 is the mole number of the solvent in a solution. If the Δw_{12} does not depend on the temperature, it follows, by virtue of Eq. (7), that χ_1 should be proportional to $1/T$. However, if χ_1 does not depend on the temperature, as here, it may be concluded from Eq. (8) that Δw_{12} should be proportional to T and that ΔH_m should become zero. These conclusions include the contradiction that such a solution is athermal; besides, the interaction parameter, χ_1, consists only of a configurational entropy change due to a solvent-solute interaction. Therefore, it is reasonable to assume that the variation in the value of χ_1 with the temperature is so slight in the temperature range of this experiment that the difference in the slope of the straight line for the different temperature could not be found.

Next, as the value of z is the ratio of the size of an asphaltene particle to that of a solvent molecule, if the molecular sizes of the solvents do not differ from one another, these values for the different systems should not differ from one another, either. The molecular sizes of benzene and the other solvents do not differ greatly; nevertheless, values of z for the asphaltene-benzene system are smaller than the others. This can probably be attributed to the fact that the values of z obtained from the intercepts of the straight lines in Figs. 2—5 are very sensitive to the length of the intercepts; we can not expect to obtain highly accurate values of z by this method. However, in order to know the order of magnitude of the molecular weight of asphaltene, we did attempt to estimate it roughly by multiplying the molecular weight of the solvent by z. For example, it was 2500 for the asphaltene-cyclohexane system and 1020 for the asphaltene-benzene system.

The lower the value of χ_1, the better the solvent. Consequently, as is shown in Table 1, chloroform is the best solvent among those used, while benzene and cyclohexane are relatively poor solvents.

The solid lines in Figs. 6—9 show the curves of the functions, which were obtained by substituting the values of χ_1 and z shown in Table 1 into Eq. (5). The observed values of activities, $a_1=p/p_0$, are also plotted

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5) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, New York (1953) Chapt. 13.

6) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

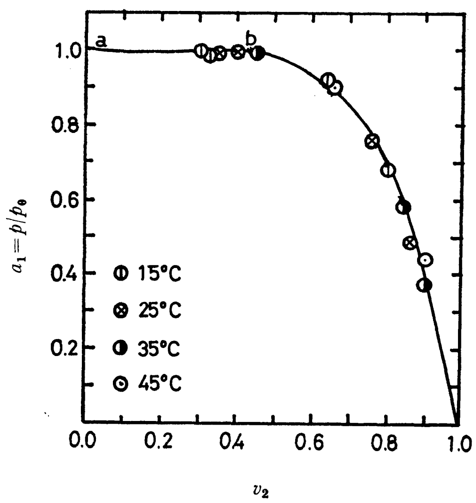

Fig. 6. An activity of cyclohexane $a_1(=p/p_0)$ in the system of asphaltene and cyclohexane *versus* the volume fraction of asphaltene v_2.

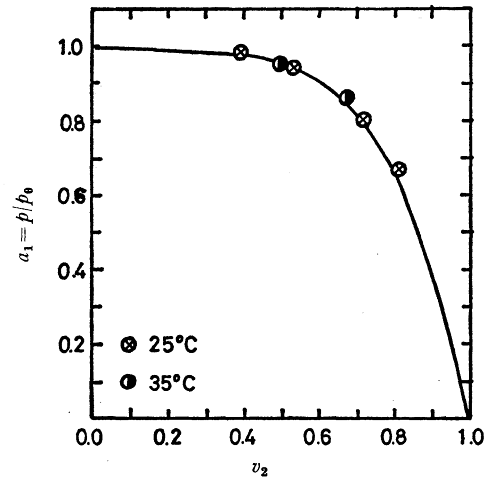

Fig. 7. An activity of benzene $a_1(=p/p_0)$ in the system of asphaltene and benzene *versus* the volume fraction of asphaltene v_2.

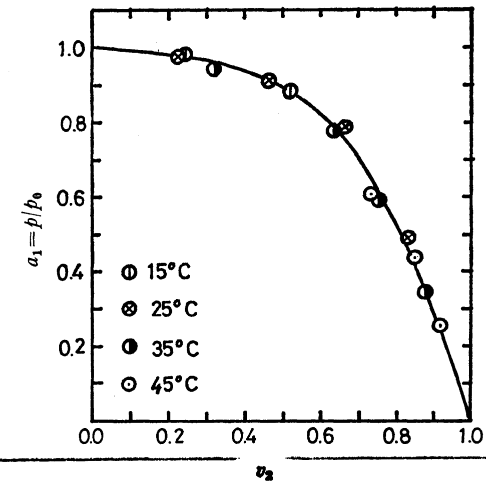

Fig. 8. An activity of chloroform $a_1(=p/p_0)$ in the system of asphaltene and chloroform *versus* the volume fraction of asphaltene v_2.

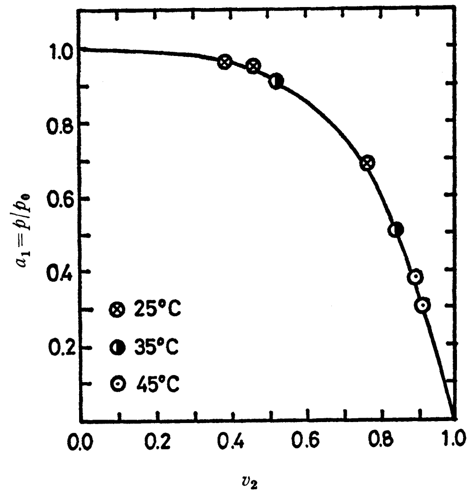

Fig. 9. An activity of carbon tetrachloride $a_1(=p/p_0)$ in the system of asphaltene and carbon tetrachloride *versus* the volume fraction of asphaltene v_2.

in these figures. Among these results, it is noteworthy that a phase separation occurs in the asphaltene-cyclohexane system, as is shown in Fig. 6, where the two different compositions of the separating phases are indicated by the symbols a and b.

The critical volume fraction and the critical interaction parameter of a phase separation are given by:

$$(v_2)_c = \frac{1}{(1+z)^{1/2}}$$

$$(\chi_1)_c = \frac{1}{2} + \frac{1}{z^{1/2}}$$

The values of $(v_2)_c$ for each system are also shown in Table 1, together with the actual values of χ_1. When $\chi_1 > (\chi_1)_c$, the phase separation occurs in a certain region of some mixture compositions. As is shown in Table 1, $\chi_1 > (\chi_1)_c$ only in the case of the asphaltene-cyclohexane system (that is, a phase separation should occur in this system), while all the other systems except the asphaltene-benzene system should be homogeneous over the range of composition. In the case of the asphaltene-benzene system, as the value of χ_1 is close to the value of $(\chi_1)_c$, and as the difference between the two values is in the range of experimental error of the values, we could not decide whether or not this system is homogeneous over the range of composition. In the case of the asphaltene-cyclohexane system, the compositions of the two separated phases were obtained by the following method. Corresponding to Eq. (1), the chemical potential of the solute is given by:

$$\mu_2 = \mu_2^\circ + \boldsymbol{RT}\ln v_2 - (z-1)\ (1-v_2) + \chi_1 z(1-v_2)^2 \quad (9)$$

where μ_2° is the chemical potential of the pure solute, while the relation between the volume fraction and the molar fraction of the solute is given by:

$$v_2 = \frac{zx_2}{1+(z-1)x_2} \quad (10)$$

From Eqs. (1), (9), and (10), the mean molar Gibbs energy of mixing in units of $\boldsymbol{RT}$ is represested by;

$$\frac{g-g^{\circ}}{\boldsymbol{R}T} = (1-x_2)\ln\frac{(1-x_2)}{1+(z-1)x_2} + x_2\ln\frac{zx_2}{1+(z-1)x_2} + \frac{\chi_1 z(1-x_2)x_2}{1+(z-1)x_2}$$

when g and g° are the mean molar Gibbs free energies of the system after and before mixing respectively, and x_2 is the molar fraction of the solute. When a separation into two phases occurs, a double tangent with two contact points can be drawn to the curve of the plots of $(g-g^{\circ})/\boldsymbol{R}T$ *vs.* x_2, and the two contact points represent the two different compositions of the two phases.[7]

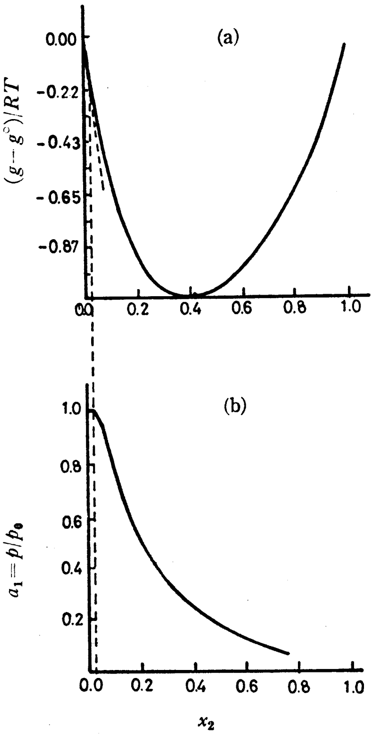

Fig. 10. Mean molar free energy of mixing asphaltene with cyclohexane, in units of $\boldsymbol{R}T$, $(g-g^{\circ})/\boldsymbol{R}T$ *versus* the mole fraction of asphaltene x_2.

The curves of these plots for the asphaltene-cyclohexane system are shown in Fig. 10(a), while the plots of $a_1=p/p_0$ *vs.* the molar fraction of the solute, x_2, are shown in Fig. 10 (b). A double tangent can be drawn to the curve in Fig. 10 (a), and it has become apparent that the composition of the dilute phase is 0.001 asphaltene relative to the molar fraction, or 3.0 vol%, while that of the concentrated phase is 0.021 relative to the molar fraction, or 40.0 vol%.

We attempted to confirm the presence of two separated phases in this system by using another method as well. That is, a mixture of asphaltene and cyclohexane (8.5% asphaltene by volume) was prepared; it was centrifuged, and then the concentration of the supernatant solution was determined. This concentration was 5.1% asphaltene by volume. This value is slightly different from that obtained from the contact point of the double tangent drawn to the curve in Fig. 10 (a), but it is evidence of the presence of a phase separation that the concentration of the supernatant solution is different from the composition of the total mixture.

As has been mentioned above, it has become apparent that separation into two phases occurs in a mixture of asphaltene with a saturated hydrocarbon such as cyclohexane; therefore, if the maltene component of asphalt, which is regarded as a solvent of asphaltene in a real asphalt, has an abundance of saturated hydrocarbon compounds, it can be guessed that the separation into the concentrated and dilute phases of asphaltene is possible at equilibrium in a real asphalt, too. Furthermore, in many cases the content of asphaltene in a straight asphalt is about 10—25% by weight; this agrees with the region of compositions in which a phase separation occurs in the asphaltene-cyclohexane system. If the fine drops of the concentrated phase of asphaltene disperse in its dilute phase, these states shall be relatively stable, because the difference in the specific weights of their phases is small and the viscosity of the dilute phase is considerably high. These states inside the asphalt can be described by saying that the asphaltene particles which adsorp a maltene component disperse in a maltene phase in which a slight quantity of asphaltene is dissolved.

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[7] H. Tompa, "Polymer Solutions," Butterworths Scientific Publications, London (1956), Chap. 2.