BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 231—232 (1979)

The Principle of Corresponding States at Elevated Pressure

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(Received June 14, 1978)

Synopsis. The principle of corresponding states was examined at elevated pressure, and the validity of the assumption that the external degrees of freedom of the solution are given by linearity in the weight fraction of the components was examined without any model by use of the superposition method.

The principle of corresponding states[1,2] has been investigated extensively. Especially, the theory of moderately concentrated polymer solution thermodynamics[3,4]has shown newer development and made great success by the aid of the free volume theory.[5] In this theory, themodynamic quantities of the solution are represented by the characteristic parameters and the interaction energy parameter. This theory emphasizes the importance of the volume dependence of the free energy, and it is the elementary problem how the quantities characterizing the properties of the mixture are related to those of the respective components.[6] In this point, several model theories have been presented,[2–4] but, it is scarce that the characteristic parameters of the mixture are determined directly form P-V-T relations of it and are compared with those of respective components.[6,7] Moreover, it is of great importance that the volume dependence of the free energy should be examined from the pressure effect.[7] In this note, we examined the validity both of the principle of corresponding states at elevated pressure and of the assumption that the external degrees of freedom of the solution are given by linearity in the weight fraction of the components by use of the superposition method.

The examined systems are nitrobenzene,[8] aniline,[8] their mixture,[9] bromobenzene,[8] chlorobenzene,[8] *trans*-decalin,[10] and poly(dimethylsiloxane)[11] for the investigation of the principle of corresponding states at elevated pressure, and nitrobenzene-aniline,[9] poly(dimethylsiloxane)-benzene,[7] and poly(isobutylene)-benzene[12] for the investigation of the assumption for the external degrees of freedom.

According to the principle of corresponding states, the equation of states is represented by

$$f(\tilde{P},\ \tilde{V},\ \tilde{T}) = 0,\quad \tilde{P} = P/P^*,\quad \tilde{V} = V/V^*,\quad \tilde{T} = T/T^*, \tag{1}$$

where tilde and asterisk signify respectively the reduced quantities and the characteristic parameters. These characteristic parameters are related to each other by the relation

$$P^*V^* = T^*S^*, \qquad S^* = ck, \tag{2}$$

where c is the external degrees of freedom, and V^* and c are expressed in per gram.

Using these relations, thermal expansion coefficient and isothermal compressibility can be made to be dimensionless and reduced as follows:

$$\begin{aligned} \alpha T &= (\partial \ln V/\partial \ln T)_P = (\partial \ln \tilde{V}/\partial \ln \tilde{T})_{\tilde{P}} = \tilde{\alpha}\tilde{T}, \\ \beta P &= (\partial \ln V/\partial \ln P)_T = (\partial \ln \tilde{V}/\partial \ln \tilde{P})_{\tilde{T}} = \tilde{\beta}\tilde{P}. \end{aligned} \tag{3}$$

Accordingly, αT and βP are the universal functions of reduced quantities and should be expressed by a master curve. Since $\tilde{P}\simeq 0$ at atmospheric pressure, because P^* for these substances are few thousands bars, αT at atmospheric pressure plotted against $\ln T$ or $\ln V$ can be superposed by shifting along the abscissa. As $\beta P = \tilde{\beta}\tilde{P}$ gives $\ln\beta = \ln\tilde{\beta} - \ln P^*$, the curves of $\ln\beta$ *vs.* $\ln T/a_{T^*}$ can be superposed by shifting along the ordinate, since for the same value of T/a_{T^*}, $\tilde{T}$ is same each other. From these shift factors, a_{T^*} from αT *vs.* $\ln T$, a_{V^*} from αT *vs.* $\ln V$, and a_{P^*} from $\ln\beta$ *vs.* $\ln T/a_{T^*}$, the ratios of the characteristic parameters to those of the reference substance are obtained:

$$a_{P^*} = P^*/P_1{}^*,\quad a_{V^*} = V^*/V_1{}^*,\quad a_{T^*} = T^*/T_1{}^*, \tag{4}$$

where 1 implies the reference substance. The ratio of the external degrees of freedom are given from these by

$$c/c_1 = a_{P^*}a_{V^*}/a_{T^*}. \tag{5}$$

Moreover, at the same value of P/a_{P^*}, αT *vs.* $\ln T/a_{T^*}$ should give the well superposed one curve. By use of a_{T^*} and a_{V^*}, the universal relation of V/a_{V^*} *vs.* T/a_{T^*} is also obtained. This correspeonds to the intersection of $f(\tilde{P},\tilde{V},\tilde{T})$ with $\tilde{T}$-$\tilde{V}$ surface of $\tilde{P}$-$\tilde{V}$-$\tilde{T}$ space. In this way, without any model theory the characteristic parameter (ratio) is determined and the principle of corresponding states at elevated pressure is examined.

The superposed curves of αT *vs.* $\ln T/a_{T^*}$ at 1, 400, and 800 bar for nitrobenzene (reference substance)—P_1 in Figs. 1 and 2—are shown in Fig. 1. They are well superposed and show that a^*'s in Eqs. 4 determined at atmospheric pressure is proper even for elevated pressure and does not change with pressure. This is shown also in Fig. 2 for the relation between T/a_{T^*} and V/a_{V^*} at various pressures. Though it is not shown in Figs. 1 and 2 (since the range of αT is beyond that of these Figs.), the superposition is well performed for poly(dimethylsiloxane)–benzene and poly(isobutylene)–benzene mixtures. Therefore, at elevated pressure the principle of corresponding states is valid and the superposition is applicable.

The relation of the external degrees of freedom for nitrobenzene–aniline, poly(dimethylsiloxane)–benzene, and poly(isobutylene)–benzene mixtures determined as the above with the weight fraction could not be expressed by linearity. For example, c/c_1 *vs.* weight fraction of aniline for nitrobenzene–aniline mixture is shown in Fig. 3. In all cases, negative discrepancy

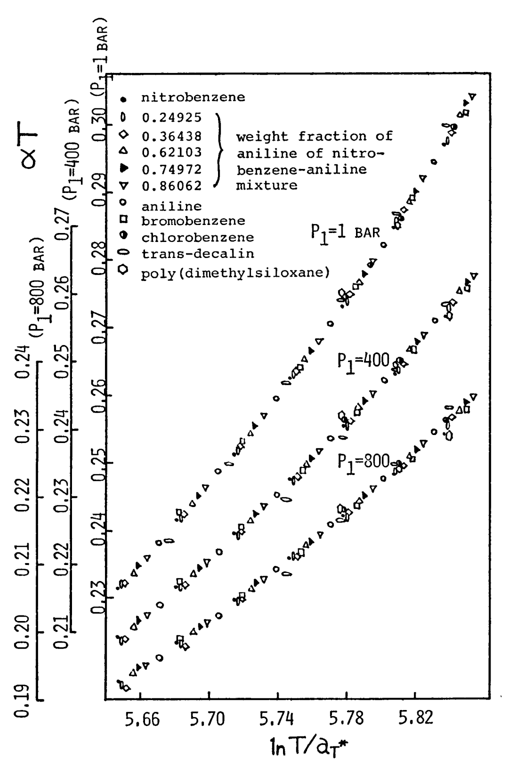

Fig. 1. The superposed curve of αT plotted against $\ln T/a_T$*. The indicated pressure, P_1, is for nitrobenzene (reference substance).

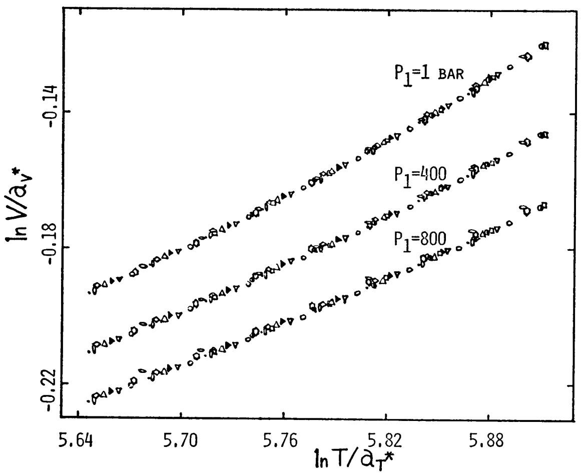

Fig. 2. The superposed curve of $\ln V/a_V$* *vs.* $\ln T/a_T$*. The symbols for the substances are same as in Fig. 1.

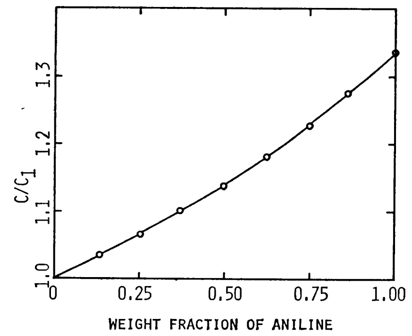

Fig. 3. The relation of the ratio of the external degrees of freedom of nitrobenzene-aniline mixture with weight fraction of aniline.

TABLE 1. CHARACTERISTIC PARAMETERS AT 30 °C AND ATMOSPHERIC PRESSURE DETERMINED BY USE OF THE NEWER FLORY THEORY

	P* (Bar)	V* (cm^3/g)	T* (K)
Nitrobenzene	7198	0.6898	5863
trans-Decalin	5063	0.9487	5726
Poly(dimethylsiloxane)	3390	0.8410	5563

was observed. In poly(dimethylsiloxane)–benzene the discrepancey is about 1.4% at 50% weight fraction and in poly(isobutylene)–benzene that is about 0.9% at 50%. This discrepancy corresponds to Q_{12}, entropy correction term of the new Flory theory.[3] This implies that the relation of the external degree of freedom with concentration much influences to the theoretical prediction for the solution thermodynamics, and the assumption of linearity is open to further consideration.

For comparison, the characteristic parameters determined by the newer Flory theory for nitrobenzene, *trans*-decalin, and poly(dimethylsiloxane) are tabulated in Table 1. These are the values obtained at 30 °C and atmospheric pressure.

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