Brønsted's Congruence Principle and Mixtures of n-Alkanes

of Widely Different Chain Lengths

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Previously reported results of an investigation of the swelling of linear polymethylenes in low-molecular n-alkanes have been applied in an attempt to test the congruence principle under extreme conditions. The mixed state of aggregation of the polymer and the difficulties in determining independently the effective index did, however, prevent a quantitative test in this region. It is suggested that the congruence principle may apply to n-alkanes only up to a certain critical index, and possible relationships above that index are discussed.

In a previous paper [1] the swelling of linear polymethylenes (polythenes) in low molecular weight alkane vapours was investigated. Since polymethylene swelled in *e.g.* n-hexane vapours is essentially a binary mixture of normal alkanes, and the phenomenon of swelling is virtually governed by the same fundamental laws of thermodynamics as the process of dissolution, it should be justified to compare the findings with earlier results reported from this laboratory on other binary mixtures of n-alkanes. In addition the polymethylene data might afford a convenient test of Brønsted's theory of congruence [2,3] under extreme conditions.

According to this theory a mixture of isochemical compounds may be characterized by its index $\nu = \Sigma x_i \cdot \nu_i$, x_i being the mole fraction and ν_i the number of carbon atoms (chain length) of a component i. Any index or "average chain length" may be reproduced in an infinite number of ways using different individual components in the required mole fractions. The principle of congruence postulates that certain thermodynamic properties are determined alone by the index of the mixture, in the sense that mixtures having the same index, *congruent mixtures*, have identical properties, although their composition may be entirely different.

Experimental evidence in support of the principle has been obtained in this laboratory by measurements comprising two properties, solubility and

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vapour pressure, and two homologous series, methyl esters of normal fatty acids ($4 \leq \nu \leq 15$) and normal alkanes ($6 \leq \nu \leq 36$). Data by J. N. Brønsted, recently reported by J. Koefoed [3] proved that the solubility of *sym*-tetra-phenylbutane was identical in an ester of a certain index ν and in binary mixtures of homologues, if only the mixtures had the same index ν. Vapour pressure measurements by Brønsted and Koefoed [2] on binary *n*-alkane mixtures ($6 \leq \nu \leq 16$) disclosed that the activity coefficient f_1 of a component 1 could be represented by the simple relation

$$\log f_1 = B \ (\nu_{12} - \nu_1)^2. \tag{1}$$

It thus depended only on the index ν_1 and on the index ν_{12} of the mixture, whereas it was independent of the index of the second compound in accordance with the congruence principle. B is a constant depending upon temperature and on the nature of the component 1. For *n*-hexane at $20°$ B is -0.00048.

In their paper [2] Brønsted and Koefoed pointed out that although the relation (1) satisfied the experimental data in the region $6 \leq \nu \leq 16$, it could not be expected to hold by unlimited increase in chain length. This appears to be confirmed by our measurements on mixtures of polymethylenes of index up to 2 860 and low molecular *n*-alkanes. As shown below these extreme mixtures do not satisfy equation (1).

Apparent activity coefficients and indices have been calculated from some of the hexane-polymethylene data. They are given in Table 1.

Table 1. Activity coefficients in mixtures of n*-hexane and polymethylene at* $22°$ C.

Series *	Film * No.	ν_P	x_6	-log f'_6	ν_{LP}	log ν_{LP}
4	10d	2 860	0.9725	0.05	84	1.92
			.9567	.17	129	2.11
			.9256	.35	218	2.34
			.8228	.70	512	2.71
			.9053	.43	276	2.44
			.8820	.51	341	2.53
			.6811	.99	916	2.96
6	1	1 430	.6736	.75	470	2.67
			.8340	.48	242	2.38
			.9202	.23	120	2.08
			.9583	.08	65	1.81
			.8760	.39	182	2.26

* Ref. 1, Table 4

The mole fraction x_6 was calculated from $x_6 = \left[1 + \dfrac{86}{M_P} \cdot \dfrac{g_P}{g_6} \right]^{-1}$ as usual.

It will be noted that, owing to the extreme ratio of the molecular weights of the components, even dilute solutions of hexane in polymethylene have large mole fractions. Thus in a 0.5% solution of *n*-hexane in polymethylene of
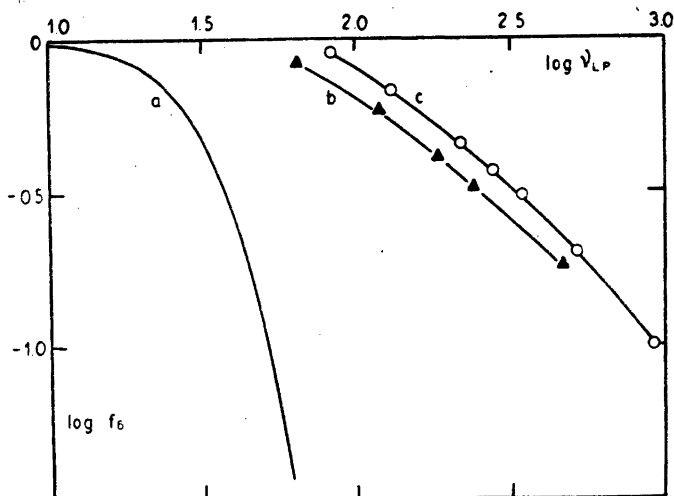
Fig. 1. Activity coefficient f_6 in n-hexane/polymethylene mixtures against the index of the mixtures. a. Extrapolated from the region $6 \leq v \leq 16$ (Brønsted and Koefoed); b, c. Experimental curves.

a molecular weight 40 000 ($v_P = 2\ 860$) the mole fraction is $x_6 = 0.7$. Log f'_6 was obtained from log $f'_6 = \dfrac{p_6}{p_{6(6)}}$ —log x_6, the necessary data being taken from Ref. 1 Table 4. For the present purpose, the deviation of the hexane vapours from ideality may be neglected, since the correction would only affect the third decimal place. The sixth column contains the index v_{LP} of the binary mixtures calculated from $v_{LP} = 6\ x_6 + (1-x_6)\ v_P$.

The experimental data from Table 1 are plotted in Fig. 1 (b, c), together with the curve a of Brønsted and Koefoed (equation 1, $B = -0.00048\ v_1 = 6$) extrapolated to higher indices. The discrepancy between prediction and experiment is evident.

It must, however, be pointed out that this does not necessarily imply any invalidation of the theory of congruence in general, it only emphasizes that this theory cannot be subjected to strict experimental test in the high polymeric region, the chief reason being the mixed state of aggregation of solid poly-methylenes, which are not even in thermodynamic equilibrium cf. ref. 1 p. 243. The dissolved low-molecular component is probably only contained in the amorphous parts of the polymer. Consequently the index of the mixture v_{LP}, calculated as above, does not represent the effective value, since the mole fraction of the polymer should not enter by its full value. Adequate correction for the presence of inactive crystalline material is not possible. It must also be borne in mind that the index and average molecular weight of polymethylene samples cannot be determined independently with any great accuracy, and finally that the presence of branched-chain material cannot be quite excluded. The difficulties arising from the mixed order-disorder state may possibly be

eliminated by working at temperatures above the melting point of poly-methylene. In this region, however, the experimental technique is complicated.

So far the theory of congruence has been neither proved nor disproved in the region of high polymer n-alkanes. A priori the mixtures investigated by us [1] might be assumed to comply with even simpler laws than that implied in the expression (1), and not to follow the principle of congruence.

Imagine an isotropic mixture of (non-volatile) polymethylene (P) and a volatile low-index n-alkane (L). The long chains of P, consisting of say 2 000 carbon atoms each, are randomly curled up, the small molecules of L filling in the cavities $cf.$ ref. 1 page 244. No appreciable change in the properties of the mixture should be expected if the polymethylene chains were each divided into two parts containing 1 000 atoms, since the relative effect of the terminal methyl groups would still be very small. The equilibrium vapour pressure over the mixture, for instance, may be assumed to remain unaltered. In other words the activity of a given low-index n-alkane in mixtures with polymethylene should be independent of the index ν_P (chain length, molecular weight) of the polymethylene, and alone depend on weight fraction and temperature.

This is contradictory to the principle of congruence, as may be realized in the following way. The process of cleavage mentioned does not affect the weight fraction and diminishes the mole fraction x_L only to a slight degree, which is easily seen from the expression $x_L = \left[1 + \dfrac{M_P}{M_L} \cdot \dfrac{g_L}{g_P} \right]^{-1}$. Since the index ν_P is reduced to half its value by the cleavage, it follows that the index of the mixture $\nu_{LP} = x_L \cdot \nu_L + x_P \cdot \nu_P$ is different before and after the cleavage. As the vapour pressure is assumed to be unaltered, we thus have two mixtures with equal equilibrium vapour pressure but differing as regard to the index, which obviously is not in accordance with the congruence principle.

When trying to verify the alternative hypothesis experimentally we run into the same difficulties as before. Nevertheless there are indications in the material which seem to favour the hypothesis. In Fig. 15 (Ref. 1, p. 266) the vapour pressure (as fractional parts of the saturation pressure) $p_6/p_{6(6)}$ is plotted against composition (weight by weight) of the mixture. The different curves represent mixtures of n-hexane and polymethylenes of the indices indicated to the right. It is striking that the vapour pressure of the mixtures n-hexane + "2 500" and n-hexane + "1 430" are nearly identical for any given weight fraction, in accordance with the above views. The curves "2 860" and "360", however depart strongly from the other ones. As pointed out pre-viously (Ref. 1, p. 266) it is reasonable to assume, that this is a result of differ-ences in crystallinity, and that all the curves would in fact coincide if the same degree of crystallinity could be secured in the various polymethylenes. This again suggests that measurements should be carried out at temperatures above the melting region of the polymer, where the latter should be isotropic or nearly so.

It is obvious that if the chain length (index) of the polymer component is repeatedly reduced by a factor two as outlined above, ultimately a critical index ν^* is reached, below which the above hypothesis does not hold any more, because the relative weight of the terminal groups will have become significant.

Unpublished measurements in this laboratory show that liquid mixtures of n-alkanes of index up to 36 satisfy equation (1) with reasonable accuracy, so that the critical index ν^* must be larger than 36. Preliminary calculations by Brønsted suggested a value $\nu^* = 54$ (unpublished).

For further elucidation of the problems outlined in this paper it would be desirable to examine liquid n-alkane mixtures containing components of indices from about 50 to about 100. Such work has been in progress in this laboratory, but it was discontinued after the death of professor Brønsted.

The basic ideas in this paper were developed in discussions between the late professor J. N. Brønsted and the author.

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