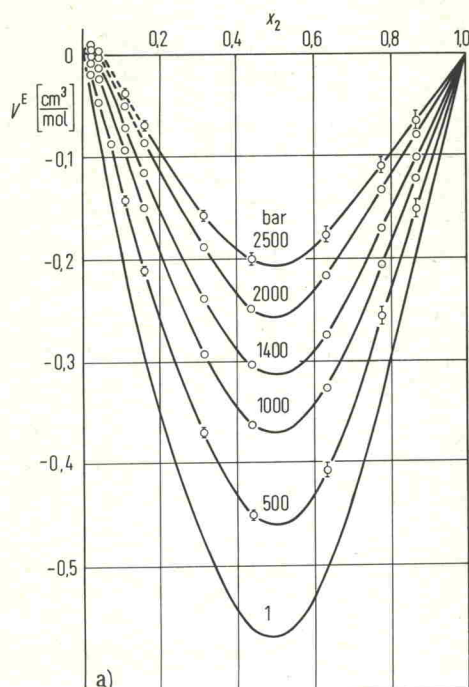


negative excess volumes occur in the interval $0.45 < x_2 < 0.5$. For illustration, the volume of mixing is plotted as a function of the molefraction x_2 for some isobars at 81.5°C in Fig. 2. In spite of the positive values for very small x_2 the shape of these curves is rather symmetric. In the concentration range $0.05 < x_2 < 0.2$ there is a point of inflection. For $x_2 > 0.7$ the graphs run linearly within the experimental error. A second point of inflection in this range is rather improbable but cannot be excluded.



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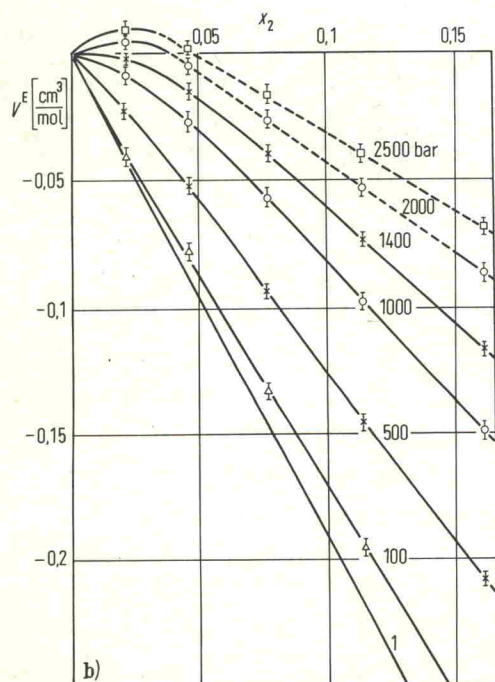


Fig. 2

Molar excess volumes V^E of the system water-3-methylpyridine at 81.5°C (x_2 = molefraction 3-methylpyridine; parameter: pressure in bar.—The dashed lines indicate the region of two coexisting liquid phases). a) complete concentration range; b) water-rich concentration range on a larger scale

Discussion

The change ΔG^E of the molar excess Gibbs energy with pressure can be easily calculated by integration of Equation (1a) at constant temperature and composition:

$$\Delta G^E = G_{(p)}^E - G_{(p_0)}^E = \int_{p_0}^p V^E dp. \quad (2)$$

The results are compiled in Table 2 and are represented for small x_2 in Fig. 3. In the last line of Table 2 the values for

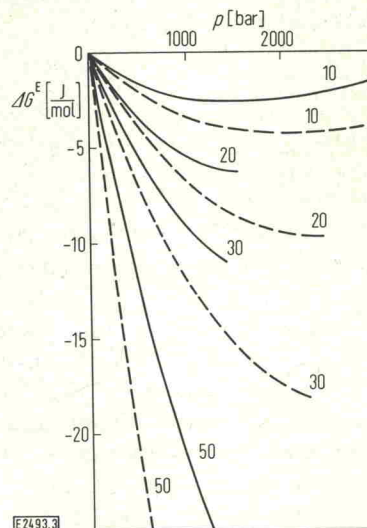


Fig. 3

Change of the molar Gibbs energy with pressure $\Delta G^E = G_p^E - G_{p=1 \text{ bar}}^E$ at 50 (dashed line) and 81.5°C (full line). Parameter: weight percent 3-methylpyridine. The curves for 20 and 30 w.% end at the phase boundary of one homogeneous phase

Table 2
 $\Delta G^E = G_p^E - G_{p=1 \text{ bar}}^E$ at 50 and 81.5°C in J mol^{-1}
 x_2 = molefraction 3-methylpyridine

$T, ^\circ\text{C}$	p , bar	10 w.% $x_2 = 0.021$	30 w.% $x_2 = 0.076$	50 w.% $x_2 = 0.162$	70 w.% $x_2 = 0.311$	90 w.% $x_2 = 0.635$
50	100	-0.5	-1.6	-3.9	-6.3	-6.3
	500	-2.2	-7.2	-17.3	-28.6	-28.6
	1500	-4.1	-15.3	-39.5	-70.7	-70.7
	2500	-4.2	-18.6	-50.9	-98.7	-98.7
81.5	100	-0.4	-1.3	-2.9	-4.8	-5.0
	500	-1.6	-5.6	-12.5	-21.6	-22.8
	1500	-2.6	—	-27.7	-52.1	-55.5
	2500	-2.0	—	—	-69.2	-76.8
81.5	1	+225.0	+595.0	+906.0	+1106.0	+850.0?

$G_{(p_0=1 \text{ bar})}^E$ at 81.5°C interpolated from literature data are given [4]**). The changes of G^E with pressure are negative and small relative to the values at 1 bar.

Since G^E is positive at normal pressure it decreases with increasing pressure.

The pressure dependence of the molar excess entropy S^E is given by Equation (3):

$$\left(\frac{\partial S^E}{\partial p} \right)_{T,x} = - \left(\frac{\partial V^E}{\partial T} \right)_{p,x}. \quad (3)$$

**) The uncertainty is evaluated by the authors to be ± 6 Joule/mol.

No numerical calculation will be presented here, since from the two isotherms for which accurate data are available, only a linear dependence of the excess volume upon temperature can be deduced, which will be a poor representation of the real behaviour. But from Equation (3) it follows immediately that $(\partial S^E/\partial p)_{T,x}$ must be negative since $(\partial V^E/\partial T)_{p,x}$ is positive. Thus, S^E being negative at normal pressure, $|S^E|$ will increase with increasing pressure, indicating an increasing deviation from ideal entropy of mixing.

The pressure dependence of the molar excess enthalpy H^E is readily obtained from Equation (4):

$$\left(\frac{\partial H^E}{\partial p}\right)_{T,x} = V^E + T \left(\frac{\partial S^E}{\partial p}\right)_{T,x} \quad (4)$$

Here, V^E is negative — except for small x_2 and high pressures — and $(\partial S^E/\partial p)_{T,x}$ is negative, too. Therefore, $(\partial H^E/\partial p)_{T,x}$ must also be negative. Since the excess enthalpy at normal pressure is negative, $|H^E|$ will increase with increasing pressure. This has been confirmed by the direct determination of the temperature change on mixing [3].

This qualitative discussion of the pressure dependence of the thermodynamic functions G^E , S^E , and H^E shows that for the system water-3-methylpyridine both H^E and S^E are negative at normal pressure and both have a similar pressure dependence indicating an increasing deviation from ideality, which finally gives rise to a phase separation. The molar excess energy G^E , however, which is equal to the difference $H^E - TS^E = G^E$, decreases with increasing pressure; this obviously shows that G^E is inappropriate as a measure of deviation from ideality for this system. From a thermodynamic point of view, however, it is the Gibbs energy G which is responsible for the phase behaviour of the system and it is interesting to note, that so small a change of G^E causes such a striking phenomenon as it is the separation into two liquid phases.

The results can be used to test some qualitative statements about the excess functions at high pressures deduced from the pressure

dependence of liquid-liquid immiscibility phenomena. 3-Methylpyridine and water are miscible in all proportions at normal pressure; with increasing pressure, however, a separation into two liquid phases is observed. Isothermal $p(x)$ -sections through the two-phase region in the T - p - x space show immiscibility loops with a lower critical solution point with respect to pressure [1]. For this type of phase behaviour the inequality

$$\left(\frac{\partial^2 V^E}{\partial x^2}\right)_c < 0 \quad (5)$$

must hold, provided that G is an analytic function at and near the critical point [2, 5]. Fig. 2b shows that inequality (5) is satisfied in the concentration range of liquid-liquid immiscibility, indicated by dashed lines. Nevertheless, it seems to be possible within the limits of experimental error that $(\partial V^E/\partial x^2)_{T,p}$ may equal zero at the critical concentration $x_2 = 0.077$ which would imply, that $(\partial^2 H^E/\partial x^2)_c$ equals zero, too [6, 7]. This is not in contradiction to experiments, since the observed temperature change on mixing, plotted as a function of x_2 , has a point of inflection in the range $x_2 < 0.2$ [3].

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