

Excess Volumes of a Binary Liquid Mixture at High Pressure

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The excess volume of the system water-3-methylpyridine has been determined by direct measurements at 50, 81.5, and 95°C up to 2500 bar. The apparatus is described.

The results are used to calculate the variation of the molar excess Gibbs energy G^E with pressure. The variation of the molar excess enthalpy H^E and the molar excess entropy S^E with pressure are discussed qualitatively.

The second derivative of the excess volume with respect to the molefraction is compared with thermodynamic conclusions derived from liquid-liquid immiscibility phenomena.

Das Exzeßvolumen des binären flüssigen Systems Wasser-3-Methylpyridin wurde bei 50, 81,5 und 95°C bis zu Drücken von 2500 bar direkt gemessen. Die Apparatur wird beschrieben.

Die Druckabhängigkeit der molaren Gibbsschen Exzeßenergie G^E wird mit Hilfe der Ergebnisse berechnet. Die Druckabhängigkeit der molaren Exzeßenthalpie H^E und der molaren Exzeßentropie S^E wird qualitativ diskutiert.

Die zweite Ableitung des Exzeßvolumens nach dem Molenbruch wird mit Aussagen verglichen, die mit Hilfe der Thermodynamik aus Flüssig-Flüssig-Entmischungserscheinungen abgeleitet werden können.

Introduction

A complete thermodynamic description of a mixture can be given if the molar Gibbs energy G is known as a function of temperature, pressure, and composition; all these variables can be determined experimentally. Other thermodynamic functions can be derived from the Gibbs energy by differentiation.

There exists a considerable body of knowledge concerning the temperature and concentration dependence of G , but little is known about the pressure dependence which is given by the relation

$$\left(\frac{\partial G}{\partial p}\right)_{T,x} = V, \quad (1)$$

V being the molar volume of the mixture.

Using the concept of the ideal liquid mixture it is sufficient to know the deviations from this type described by the excess functions; the molar excess Gibbs energy is defined by

$$G^E = G_{\text{real}} - G_{\text{ideal}}$$

In analogy to Equation (1) we have

$$\left(\frac{\partial G^E}{\partial p}\right)_{T,x} = V^E \quad (1a)$$

where V^E is the molar excess volume of the mixture or the molar volume change on mixing. Thus the determination of the excess volume as a function of pressure, temperature, and composition yields the information needed to calculate the pressure dependence of the thermodynamic excess functions G^E, H^E, S^E , etc.

Table 1
Excess volumes of the system water-3-methylpyridine at 50, 81.5, and 95°C in $\text{cm}^3 \text{mol}^{-1}$

x_2 = molefraction 3-methylpyridine, bracketed numbers = error of the last figure. A superscript * indicates the region of two coexisting liquid phases

$T, ^\circ\text{C}$	p, bar	10 w.% $x_2 = 0.021$	20 w.% $x_2 = 0.046$	30 w.% $x_2 = 0.076$	40 w.% $x_2 = 0.114$	50 w.% $x_2 = 0.162$	70 w.% $x_2 = 0.311$	80 w.% $x_2 = 0.436$	90 w.% $x_2 = 0.635$	95 w.% $x_2 = 0.786$
50	100	-0.050 (3)	-0.103 (4)	-0.162 (4)	-	-	-	-	-	-
	500	-0.033 (3)	-0.073 (4)	-0.118 (4)	-	-0.268 (5)	-0.501 (7)	-0.605 (8)	-0.511 (8)	-0.305 (8)
	800	-0.023 (3)	-0.056 (3)	-0.095 (4)	-	-0.225 (5)	-0.445 (6)	-0.545 (7)	-0.455 (8)	-
	1000	-0.017 (3)	-0.046 (3)	-0.080 (4)	-	-0.202 (4)	-0.410 (6)	-0.508 (7)	-0.420 (8)	-0.246 (8)
	1300	-0.011 (3)	-0.034 (3)	-0.062 (5)	-	-0.174 (5)	-0.364 (8)	-0.455 (9)	-0.370 (9)	-
	1600	-0.007 (3)	-0.022 (3)	-0.046 (4)	-	-0.148 (5)	-0.326 (8)	-0.407 (9)	-0.326 (9)	-0.193 (9)
	1900	-0.002 (3)	-0.013 (3)	-0.035 (4)	-	-0.128 (5)	-0.290 (8)	-0.365 (9)	-	-
	2000	-	-	-	-	-	-	-0.352 (9)	-0.278 (9)	-0.164 (9)
	2200	+0.002 (3)	-0.007 (3)	-0.025 (4)	-	-0.109 (5)	-0.260 (7)	-0.328 (8)	-	-
	2500	+0.006 (3)	-0.001 (3)	-0.020 (4)*	-0.052 (4)*	-0.096 (5)	-0.235 (7)	-0.298 (8)	-0.230 (9)	-0.135 (9)
	81.5	100	-0.040 (3)	-0.077 (3)	-0.132 (4)	-	-	-	-	-
500		-0.023 (3)	-0.051 (3)	-0.091 (3)	-0.145 (4)	-0.208 (5)	-0.368 (6)	-0.445 (7)	-0.403 (8)	-0.250 (8)
800		-0.013 (3)	-0.036 (3)	-0.068 (3)	-	-0.170 (4)	-0.316 (6)	-0.390 (7)	-0.352 (7)	-0.215 (8)
1000		-0.008 (3)	-0.027 (3)	-0.056 (3)	-0.097 (4)	-0.148 (4)	-0.289 (6)	-0.360 (7)	-0.323 (7)	-0.197 (8)
1200		-0.004 (3)	-0.019 (3)	-0.046 (3)	-	-0.131 (5)	-0.263 (7)	-0.328 (8)	-0.296 (8)	-0.180 (9)
1400		-0.001 (3)	-0.014 (3)	-0.039 (3)	-0.071 (3)	-0.116 (5)	-0.232 (7)	-0.301 (8)	-0.273 (8)	-0.165 (9)
1600		+0.002 (3)	-0.010 (3)	-	-	-0.104 (5)	-0.217 (7)	-0.278 (8)	-0.250 (8)	-0.152 (9)
2000		+0.005 (3)	-0.004 (3)*	-0.026 (3)*	-0.053 (3)*	-0.085 (4)	-0.186 (6)	-0.238 (7)	-0.212 (8)	-0.128 (9)
2500		+0.010 (3)	+0.002 (3)*	-0.017 (3)*	-0.038 (3)*	-0.068 (4)*	-0.156 (6)	-0.198 (7)	-0.175 (7)	-0.105 (8)
95		1000	0.00 (1)	0.00 (1)	-0.02 (2)	-	-	-	-0.30 (5)	-
	2000	0.00 (1)	0.00 (1)	-0.01 (2)	-	-	-	-0.20 (5)	-	-
	2500	0.00 (1)	0.00 (1)	-0.01 (2)	-	-	-	-0.15 (5)	-	-

The system investigated, water-3-methylpyridine, was chosen since earlier experiments on the pressure dependence of liquid-liquid immiscibility phenomena suggested a significant change of the volume of mixing with increasing pressure [1, 2].

Experimental

Apparatus: The excess volumes were determined by direct measurement of the volume changes on mixing the two pure components [3]. The mixing device was constructed as a pycnometer: the volume changes of the liquid enclosed in the mixing device were determined by the displacement of a piston in a cylindrical tube of small cross section, the volume of the cylindrical tube being small

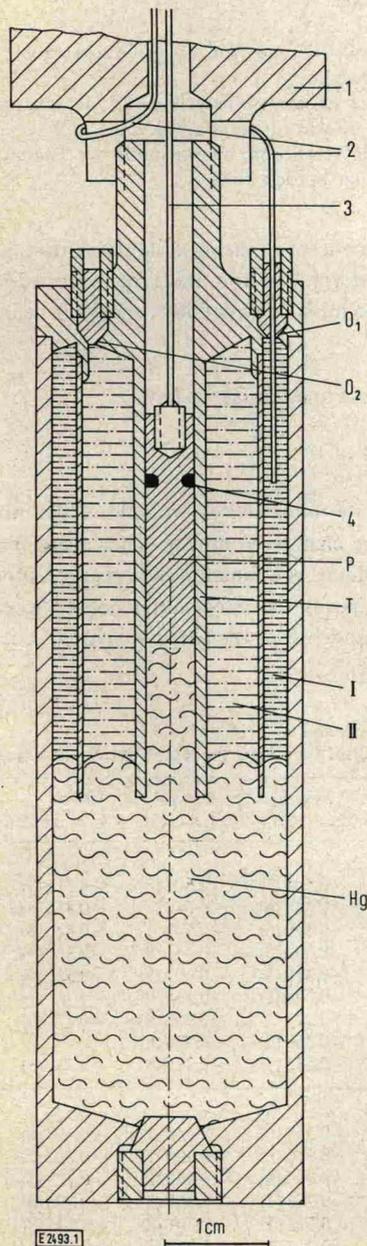


Fig. 1

Device for the direct determination of excess volumes.
1 = sealing flange of the autoclave, 2 = miniature steel-walled thermocouple, 3 = wire for the inductive coil, 4 = viton O-ring.
For further explanation see text

relative to the total volume of the mixing device. Inside, the upper part of the mixing vessel is divided into two concentric sections I and II by means of a thin tube (see Fig. 1). The mixing vessel is filled with mercury until the two concentric sections form chambers separated one against the other. These chambers can be charged with the pure components through the sealable openings O_1 and O_2 . The tightly fitted piston P can move freely in the inner tube T that is carefully honed. The piston separates the liquid inside the vessel against the pressure transmitting medium. Volume changes of the liquid enclosed in the vessel cause the piston to move. Its position can be detected by an inductive coil.

The mixing vessel is mounted into a high-pressure autoclave; so it has not to withstand any pressure differences. For mixing the two liquid components, the whole autoclave is turned upside down: the components are dislodged from the chambers by the mercury and do mix in the lower part of the vessel.

Pressure: The pressure plant was built up with commercially available high pressure equipment. The pressure was generated with a manually operated pressure generator; the pressure transmitting medium was liquid water. The pressure was determined with bourdon gauges.

Temperature: The autoclave was thermostated by direct contact with a recycled thermostated liquid. The constancy of temperature was obtained by arranging two thermostats in a series. The temperature was controlled with a platinum resistance thermometer. Temperature changes accompanying the mixing process could be detected by a miniature steelwalled thermocouple installed in the mixing vessel.

Materials: 3-Methylpyridine was purified by fractional distillation; the index of refraction of the samples was $n_D^{20} = 1.5067 \pm 1$; no impurities were detected by gaschromatographic analysis with TWEEN 20 and polyethyleneglycol CW 1000 as stationary phases. H_2O was freshly distilled, also Hg used for the separation of the two components in the mixing vessel.

Accuracy: Temperature: Constancy better than $0.01^\circ C$, accuracy better than $0.2^\circ C$. Pressure: Accuracy better than ± 1 bar (range 1–1000 bar) and ± 3 bar (range 1000–2500 bar).

Inductive coil: a displacement of 0.001 mm could be detected.

Volume: The excess volume was calculated from the piston displacement according to

$$V^E = \frac{h \cdot A \cdot M_1 M_2}{m_1 M_2 + m_2 M_1}$$

with h = displacement of the piston caused by the mixing process, A = cross sectional area of the piston, M_1, M_2 = molar masses, m_1, m_2 = masses of the components.

The accuracy is: $\Delta h = \pm 0.04$ mm; $\Delta A = \pm 0.25$ mm² (A being different for the different vessels used: 22–23 mm²); $\Delta m_1 = \Delta m_2 = \pm 2.0$ mg.

The maximum error of the excess volumes including the error of pressure and temperature readings are given in brackets in Table 1.

Results

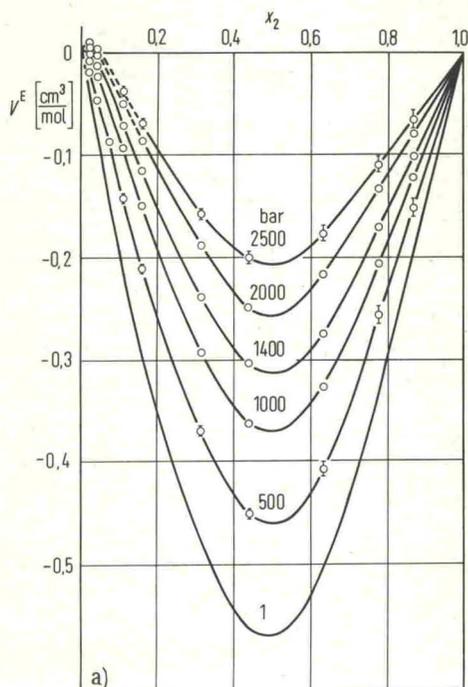
The excess volumes calculated from the piston displacements are shown in Table 1 for pressures up to 2500 bar for three different temperatures (50, 81.5, and $95^\circ C$). The measurements at $95^\circ C$ are less accurate because of the noticeable friction of the viton O-ring of the piston at this temperature. Therefore, only orientational measurements have been performed at this temperature.

The excess volumes are negative, their absolute values decrease with increasing pressure. At $81.5^\circ C$ the absolute values of the excess volumes are smaller than at $50^\circ C$ at the same pressure and molefraction.

For the mixture having a molefraction $x_2 = 0.021$ of 3-methylpyridine, the excess volumes are slightly positive for pressures above 2000 bars, the maximum value being $+0.01$ cm³/mol*).

* Positive excess volumes both at very high and additionally at very low water contents have been reported for the system pyridine-water at 1013 bar [8]; this could not be confirmed by direct measurement [9].

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 unprobable but cannot be excluded.



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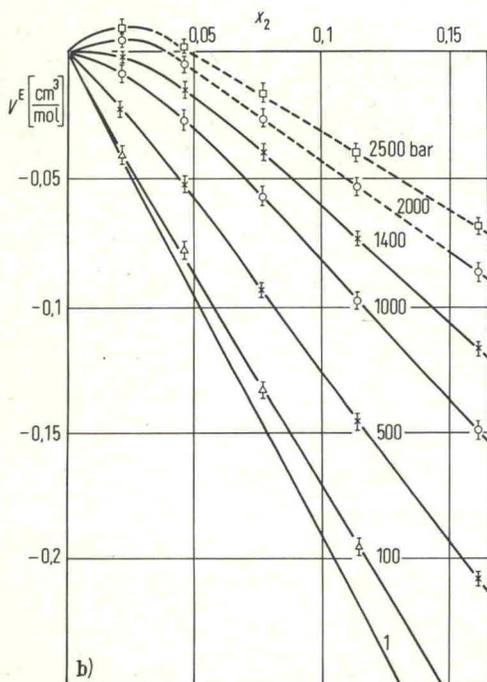


Fig. 2

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:

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

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

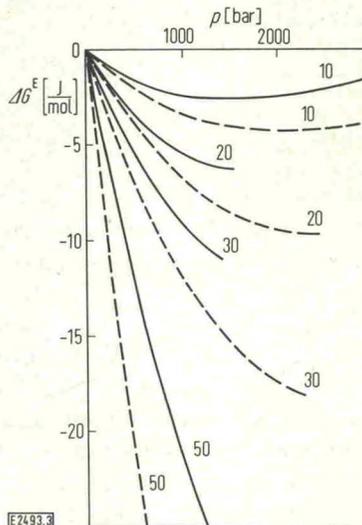


Fig. 3

Change of the molar Gibbs energy with pressure $\Delta G^E = G^E_p - G^E_{p=1 \text{ bar}}$ 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
 $\Delta G^E = G^E_p - G^E_{p=1 \text{ bar}}$ at 50 and 81.5°C in J mol^{-1}
 x_2 = molefraction 3-methylpyridine

$T, ^\circ\text{C}$	p, bar	x_2				
		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*

$G^E_{(p_0=1 \text{ bar})}$ 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):

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

***) 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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References

- [1] G. M. Schneider, Z. physik. Chem. NF. 37, 333 (1963); 39, 187 (1963).
- [2] G. M. Schneider, Ber. Bunsenges. physik. Chem. 70, 497 (1966).
- [3] P. Engels, Thesis, Karlsruhe 1970.
- [4] R. J. L. Andon, J. D. Cox, and E. F. G. Herington, Trans. Faraday Soc. 53, 410 (1957).
- [5] G. Rehage, Z. Naturforsch. 10a, 316 (1955); J. S. Rowlinson, Liquids and Liquid Mixtures, 2nd ed., London 1959.
- [6] J. S. Rowlinson, in: Critical Phenomena, Misc. Publ. Bur. Stand. No. 273, Washington 1965.
- [7] D. B. Myers, R. A. Smith, J. Katz, and R. L. Scott, J. phys. Chem. 70, 3341 (1966).
- [8] S. D. Hamann and F. Smith, Austral. J. Chem. 24, 2431 (1971).
- [9] G. Götze, Diplomarbeit, Bochum 1972.