[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vapor–Liquid Equilibrium. VI. Benzene–Methanol Mixtures[1]

BY GEORGE SCATCHARD, SCOTT E. WOOD[2] AND JOHN M. MOCHEL[3]

The second paper[4] of this series concerned the vapor–liquid equilibrium of chloroform–ethanol mixtures. The increase of the enthalpy on mixing was found to be positive in the chloroform-rich solutions and negative in the ethanol-rich solutions, the excess increase of the entropy over that of an ideal solution of the same composition on mixing at constant pressure was positive for the chloroform-rich solutions and negative for the ethanol-rich solutions, and the excess increase of the free energy over that of an ideal solution of the same composition on mixing at constant pressure was found to be positive over the entire concentration range. In Papers III, IV, and V[5] the vapor–liquid equilibria were reported for the cycle of binary systems with the components: benzene, cyclohexane, and carbon tetrachloride. The thermodynamic properties of these three systems were much simpler than for the chloroform–ethanol system, the increase of the enthalpy on mixing, the excess entropy of mixing, and the excess free energy of mixing all being positive over the whole range of concentrations. It was of interest then to compare the properties of binary systems composed of these non-polar components and an alcohol.

Experimental

Synthetic methanol was purified by distillation in the column described in III. Water vapor was excluded during the distillation by passing dry nitrogen through the column at all times. The purified methanol was stored in a dry box protected by dry nitrogen. The density of the methanol at 25° was 0.78654 g. per cc., compared to 0.78650 given by Jones and Fornwalt.[6] The benzene was purified as described in III. The vapor pressure of the purified product agreed within the experimental accuracy with the equation given in IV.

New pycnometers were used in determining the relation between the density and composition. They were single armed pycnometers having a capacity of about 10 cc. made of Jena 16-III glass.[7] The capillary had a 1-mm. bore and was

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Atlantic City, N. J., April 10, 1946.

(2) Present address: Yale University, New Haven, Connecticut.

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(4) G. Scatchard and C. L. Raymond, THIS JOURNAL, 60, 1278 (1938).

(5) G. Scatchard, S. E. Wood and J. M. Mochel, III, J. Phys. Chem., 43, 119 (1939); IV, THIS JOURNAL, 61, 3206 (1939); V, 62, 712 (1940).

(6) G. Jones and H. J. Fornwalt, 60, 1683 (1938). A summary of the best values is given in this paper.

(7) E. R. Smith and M. Wojciechowski, Roczniki Chem., 16, 104 (1936); L. G. Longsworth, THIS JOURNAL, 59, 1483 (1937).

graduated in mm. for a length of 1 cm. near the top. The arm was closed with an outside cap. They were filled by means of a hypodermic syringe fitted with a stainless steel cannula of the appropriate size and length. In order to reduce the systematic error encountered in these measurements in the previous work, the solutions were made up in 50-ml. Kimble glass volumetric flasks. The liquids were transferred by means of the hypodermic syringes. On adding the second component the tip of the cannula was held just above the surface of the first liquid. In this way the weight of the vapor displaced by the cannula is very small and the vapor displaced on the addition of the second component is practically pure in the first component and its weight can be estimated.

The vapor pressure measurements with methanol and with the solutions were made with the same apparatus as described previously. Helium was used as the confining gas. The vapor pressure of methanol was determined at 5° intervals from 25 to 65°. The equation fitted to these data is ($T = 273.16 + t$)

$$\log p = 7.98963 - 1499.361/T - 76225/T^2 \quad (1)$$

The normal boiling point calculated according to this equation is 64.51°, which is in good agreement with 64.46° given by Butler, Thomson and McLennan.[8]

In the measurement of the vapor–liquid equilibrium at a mole fraction of methanol between 0.02 and 0.05 a steady state could not be attained. It was found that the boiling temperature was extremely sensitive to the distribution of the components between the various regions of liquid and vapor in the boiling apparatus. This is due to the marked dependence of the boiling point on the composition of the liquid and also to the large difference between the composition of the liquid and vapor. At these concentrations the pressure was adjusted so as to keep the boiling temperature within 0.05° of the desired temperature for at least an hour. The run was then stopped and samples taken.

The compositions were determined from the densities at 25° which are given by the equation

$$1/d = w_1/d_1 + w_2/d_2 + \delta \quad (2)$$

in which d_1 and d_2 are the densities of the pure components and w_1 and w_2 are their weight fractions. The subscript 1 indicates methanol, and 2 benzene. Table I gives the weight fractions and mole fractions of methanol, the measured densities, δ, and the measured values of $100 V^M/V^0$. V is the volume of the mixture, V^0 that of the unmixed

(8) J. A. V. Butler, D. W. Thomson and W. H. McLennan, J. Chem. Soc., 674 (1933).

components, and $V^M = V - V^0$. It will be noticed that V^M/V^0 is quite small and has both positive and negative values. The quantity, δ, used in determining the compositions was read from a large scale graph of the values given in Table I. These density–composition results agree quite well with those of Washburn and Lightbody[9] and Schmidt.[10]

TABLE I

DENSITIES OF BENZENE–METHANOL MIXTURES AT 25°

Wt. fract. CH$_3$OH	Mole fract. CH$_3$OH	d	δ	$100V^M/V^0$
0.0000	0.0000	0.87368	....	.....
.0761	.1673	.86606	+0.00041	+0.035
.1300	.2670	.86103	+ .00033	+ .028
.1998	.3783	.85461	+ .00021	+ .017
.2959	.5060	.84598	− .00004	− .004
.4107	.6295	.83586	− .00029	− .024
.4126	.6313	.83572	− .00032	− .027
.5464	.7460	.82412	− .00045	− .037
.7443	.8765	.80741	− .00043	− .035
1.0000	1.0000	.78654	....	....

Measurements of the vapor–liquid equilibria of this system were made at intervals of approximately one-eighth in the mole fraction of the whole system at 35 and 55° and for approximately equal molal mixtures at 25 and 45°. The thermodynamic functions were calculated in terms of the excess increase of these functions over that of an ideal solution of the same concentration on mixing at constant pressure by means of the equations developed in II. These are

$$\mu_1^E = RT \ln Py_1/P_1x_1 + (\beta_1 - V_1)(P - P_1) \quad (3)$$

and

$$\mu_2^E = RT \ln Py_2/P_2x_2 + (\beta_2 - V_2)(P - P_2) \quad (4)$$

in which x is the mole fraction in the liquid phase, y the mole fraction in the vapor phase, P the vapor pressure of the solution, P_1 and P_2 the vapor pressures of the pure components, V_1 and V_2 their molal volumes as pure liquids, and β the limit at zero pressure of the difference between the molal volume of the vapor and that of a perfect gas at the same temperature and pressure. It follows from these equations with the assumption that F_x^E is linear with the temperature that

$$F_x^E = x_1\mu_1^E + x_2\mu_2^E \quad (5)$$

$$S_x^E = (F_x{}^E{}_{35°} - F_x{}^E{}_{55°})/20 \quad (6)$$

$$H_x^M = F_x^E + TS_x^E \quad (7)$$

$$F_x^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + F_x^E \quad (8)$$

In these calculations the vapor pressure of the pure components in mm. at 25, 35, 45 and 55° are: benzene, 95.98, 148.17, 223.49 and 327.10; methanol, 126.91, 209.61, 334.20 and 516.20. The values of β in cc. at these temperatures are: benzene, −2265, −1966, −1724 and −1525; methanol, −963, −848, −754 and −675. That of methanol is the value calculated by the theory of corresponding states from the equation

(9) E. R. Washburn and A. Lightbody, J. Phys. Chem., **34**, 2701 (1930).

(10) G. C. Schmidt, Z. phys. Chem., **121**, 221 (1926).

of Keyes, Smith and Gerry[11] for water vapor. It was not multiplied by 0.9 as for the non-polar liquids because of the resemblance of methanol to water. The molal volumes were calculated from the expansion equations given in the "International Critical Tables."

Smoothed Values

No simple equation, whose coefficients were determined by the method of least squares, was found that did not introduce an inflection in the curve of F_x^M plotted as a function of the mole fraction. Such an inflection would indicate the formation of two liquid phases since a line could be drawn tangent to the curve at two points.[12] Consequently the coefficients obtained by the method of least squares were adjusted at each temperature in such a manner that the inflection was removed but that minimum changes were made in F_x^E for solutions having a mole fraction of methanol of 0.5 or greater and that the values of H_x^M and S_x^E remained consistent. Equations in mole fractions were found preferable to those in volume fractions. Expressed in symmetrical form,[13] the equation used is

$$F_x^E = 4A_{1112}x_1^3x_2 + 6A_{1122}x_1^2x_2^2 + 4A_{1222}x_1x_2^3 \quad (9)$$

with the parameters given by the equations

$$A_{1112} = 167.46 + 0.463T \quad (10)$$

$$A_{1122} = 106.54 + 0.716T \quad (11)$$

$$A_{1222} = 552.54 - 0.498T \quad (12)$$

The experimental measurements are given in

TABLE II

VAPOR PRESSURE OF BENZENE–METHANOL MIXTURES

x_{CH_3OH}	y_{CH_3OH}	Dev. in y	P	Dev. in P	F_x^E	Dev. in F_x^E
			35°			
0.0242	0.2733	−0.003	203.29	+ 1.9	44.85	+7.9
.0254	.3128	+ .030	211.10	+ 7.6	37.86	−0.9
.1302	.4858	− .018	274.25	− 6.4	166.92	+2.6
.3107	.5304	+ .005	288.47	− 0.4	274.62	−3.5
.4989	.5546	+ .008	292.50	+ 0.8	300.65	+0.6
.5191	.5571	+ .006	292.70	+ 0.8	298.96	+1.1
.6305	.5790	− .001	292.49	+ 1.0	274.06	+1.9
.7965	.6421	− .008	283.58	+ 2.1	190.04	+0.2
.9197	.7688	+ .006	255.82	− 1.5	88.38	−0.6
			55°			
0.0304	0.3019	+0.006	465.84	+ 9.0	52.38	+7.3
.0493	.4051	+ .029	527.12	+16.4	63.71	−6.9
.1031	.4841	+ .005	597.48	0.0	129.96	−4.6
.3297	.5540	+ .001	664.24	− .4	284.47	−0.8
.4874	.5845	+ .006	675.62	− .1	304.49	−1.4
.4984	.5858	+ .005	675.99	+ .2	304.06	−1.2
.6076	.6078	+ .001	678.44	− .2	285.52	−0.5
.7898	.6716	− .004	664.91	− .1	198.91	−1.3
.9014	.7697	+ .005	622.29	− 3.1	109.21	−0.6
			25°			
.4742	.5343	+0.013	182.70	− 1.1	297.48	−1.8
			45°			
.5234	.5752	+0.005	451.98	+ 1.1	302.24	+2.1

(11) F. G. Keyes, L. B. Smith and H. T. Gerry, Proc. Am. Acad. Arts Sci., **70**, 319 (1936).

(12) J. Willard Gibbs, "Collected Works," Vol. I, Longmans, Green and Co., New York, N. Y., p. 118.

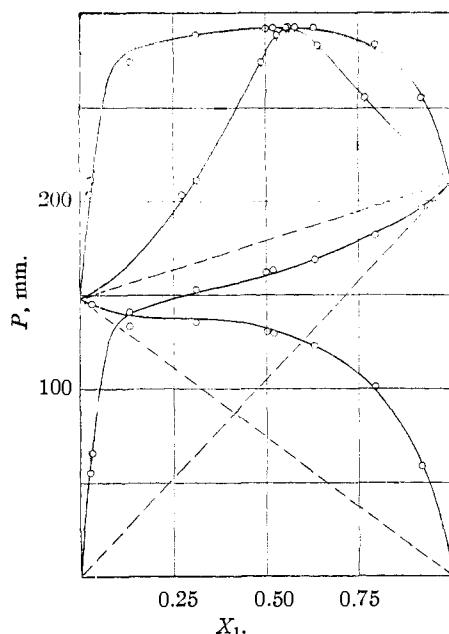(13) M. Benedict, C. A. Johnson, E. Solomon and L. C. Rubin, Trans. Am. Inst. Chem. Engrs., **41**, 371 (1945).

Fig. 1.—Vapor pressure *vs.* mole fraction for benzene-methanol at 35°.

Table II in the order of the mole fraction of methanol in the liquid phase, the mole fraction of methanol in the vapor phase, the total vapor pressure in mm., and the excess free energy change on mixing in cal. per mole. Adjacent to the last three columns the deviations of the corresponding quantities, calculated by equations 3, 4, 9, 10, 11 and 12, from the observed quantities are also listed. The results at 35° are shown in Fig. 1 in which the total pressure and the partial pressures plotted against the mole fraction of the liquid phase are represented by circles and the total pressures plotted against the mole fraction of the vapor phase are represented by flagged circles. The solid lines give the corresponding calculated values and the dotted lines show the behavior of the system according to Raoult's law.

The smooth values of the excess change of the free energy on mixing at 35°, the heat of mixing, and 308.16 times the excess change of the entropy on mixing, all expressed in cal. per mole, are given in Table III.

TABLE III

SMOOTH VALUES OF THE THERMODYNAMIC FUNCTIONS IN CAL.

x_1	F_{x350}^E	H_x^M	308.16 S_x^E	$\dfrac{308.16}{(S_v^E - S_p^E)}$	$E_v^M - H_p^M$
0.1	133	167	+ 34	−3	−3
.2	222	247	+ 25	−3	−2
.3	274	268	− 6	−2	−2
.4	299	254	− 45	−1	−1
.5	300	220	− 80	0	0
.6	282	180	−102	+1	+1
.7	244	139	−105	+2	+2
.8	187	99	− 88	+2	+2
.9	108	56	− 52	+1	+1

The uncertainty in F_x^E at 35 and 55° and half mole fraction is estimated to be about 1 cal. This would cause uncertainties of about 0.1 cal. per deg. in S_x^E and about 31 to 33 cal. in TS_x^E and H_x^M. The uncertainties in these quantities for solutions richer in methanol are probably somewhat smaller than these estimates. It is for this reason that the values of the latter two quantities are given to 1 cal. in Table III and the deviations in the excess change of the free energy listed in Table II are given to 0.1 cal. The increase of the volume on mixing at constant pressure is quite small, making the difference between the change of the thermodynamic functions on mixing at constant volume and on mixing at constant pressure very small.[14] These differences are smaller than the uncertainties in F_x^E, H_x^M and S_x^E, and consequently can be neglected. The differences between the excess change of the entropy on mixing at constant volume and at constant pressure and between the energy of mixing at constant volume and the heat of mixing at constant pressure are also given in Table III.
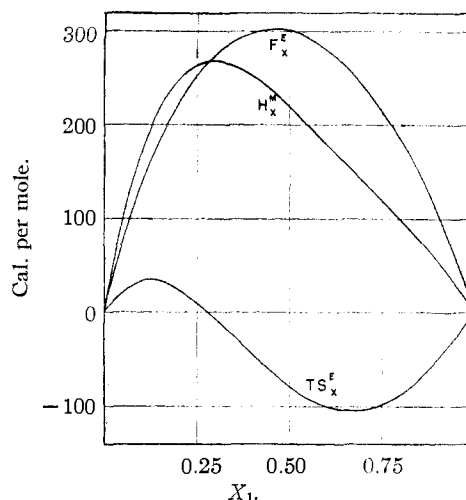

Fig. 2.—Various thermodynamic functions for benzene-methanol at 35°.

The smooth values of F_x^E and TS_x^E at 35° and H_x^M are shown in Fig. 2. The excess change of the free energy on mixing is fairly symmetrical and remains positive over the whole range of composition. The heat of mixing is also positive over the whole range of composition but it is quite unsymmetrical, the maximum occurring at approximately 0.3 mole fraction of ethanol. These values are somewhat higher than those reported by Schmidt[15] but the unsymmetrical nature of the curve is the same. The excess change of the entropy on mixing is positive up to about 0.3 mole fraction in ethanol and then becomes negative for solutions richer in alcohol. These results are discussed in the following paper.

(14) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).
(15) G. C. Schmidt, *Z. physik. Chem.*, **121**, 221 (1926).

Summary

The vapor–liquid equilibrium pressures and compositions of benzene–methanol mixtures have been measured at approximately each eighth mole fraction at 35 and 55° and for approximately equimolal mixtures at 25 and 45°. The densities have been determined at 25°.

The excess change of the free energy, enthalpy, and entropy have been calculated and expressed analytically. The excess free energy change is positive over the entire range of composition and is quite symmetrical. The change of enthalpy is positive over the entire range of composition but is quite unsymmetrical, the maximum occurring at a mole fraction of about 0.3 in methanol. The excess entropy change is positive for solutions have a mole fraction up to about 0.3 in methanol and then becomes negative.

Vapor–Liquid Equilibrium. VII. Carbon Tetrachloride–Methanol Mixtures[1]

BY GEORGE SCATCHARD, SCOTT E. WOOD[2] AND JOHN M. MOCHEL[3]

The present paper continues the measurement of the vapor–liquid equilibrium of solutions of methanol with the non-polar substances previously studied. The purification of the carbon tetrachloride was carried out as described in paper IV[4] of this series. The methanol was of the same material used for the measurements on the benzene–methanol system, VI.[5] The vapor pressure of carbon tetrachloride agreed with the values calculated by the equation given in IV within the experimental error.

Experimental

The apparatus and procedure for the density–composition measurements were the same as described in VI.[5] Due to the high molecular weight of carbon tetrachloride it was found necessary to correct the observed weight of the component first weighed in making up the solutions for the weight of the vapor displaced on addition of the second component. The results are shown in Table I in which are given the weight fraction and mole fraction of methanol, the observed density, δ, defined by equation VI-2,[6] and $100 \, V^M/V^0$. The absolute values of V^M/V^0 for this system are somewhat larger in the methanol poor solutions and about five times larger in the methanol rich solutions than for the benzene–methanol system. The compositions of the vapor and liquid samples in the vapor pressure measurements were determined from their densities by Eq. VI-2, δ being read off from a large scale graph of the observed δ quantities versus the density.

The vapor–liquid equilibrium measurements were made at intervals of approximately one-

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(4) G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **61**, 3206 (1939).

(5) G. Scatchard, S. E. Wood and J. M. Mochel, ibid., **68**, 1957 (1946).

(6) Equation numbers beginning with VI refer to the preceding paper.

TABLE I

DENSITIES OF CARBON TETRACHLORIDE–METHANOL MIXTURES AT 25°

Wt. fract. CH₃OH	Mole fract. CH₃OH	d	δ	$100 V^M/V^0$
0.0000	0.0000	1.58452	....	.....
.0296	.1276	1.53764	+0.00032	+0.049
.0640	.2472	1.48731	+ .00026	+ .039
.1326	.4233	1.39691	− .00015	− .021
.1736	.5022	1.34781	− .00035	− .047
.2379	.6252	1.25715	− .00076	− .095
.2597	.6274	1.25526	− .00071	− .089
.3874	.7523	1.13928	− .00144	− .164
.3927	.7564	1.13472	− .00138	− .156
.5987	.8775	0.98697	− .00126	− .124
1.0000	1.0000	0.78654	....	.....

eighth mole fraction of the whole system at 35 and 55° and for approximately equi-molal mixtures at 25 and 45°, using the same apparatus and procedure described in the earlier papers.[5] As in the attain a steady state for those mixtures whose mole fraction of methanol in the whole system was 0.125 and 0.25 due to the extreme sensitivity of the boiling point to the composition of the liquid and the extreme sensitivity of this composition to the distribution of methanol in the various parts of the equilibrium still. For these mixtures the pressure was adjusted to maintain the temperature within 0.05° of the desired temperature for at least an hour.

The excess change in the free energy on mixing at constant pressure over that of an ideal solution of the same concentration was calculated from the observed vapor pressure and the equilibrium mole fractions of the vapor and liquid phases using the equations given in VI. The vapor pressures of carbon tetrachloride in mm. used in these calculations are 113.88, 174.47, 258.94 and 373.53 at 25, 35, 45 and 55°, respectively. The limits at zero pressure of the difference between the molal volume of the vapor and that of an ideal gas at the same temperature and pressure are −2290, −1992, −1749 and −1549 at 25, 35, 45 and 55°,