cose was dissolved in 100 ml. of warm, absolute methanol. Crystallization was effected on slow solvent removal in a desiccator over sulfuric acid. Pure material was obtained on recrystallization (or elution) from methanol or ethanol and drying was effected under reduced pressure over phosphorus pentoxide at 56°; m. p. 112–113.5°, $[\alpha]^{20}\text{D}$ 0° (no mutarotation). It crystallized as fine needles.

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.66. Found: C, 39.90; H, 6.72.

α-D,α-L-Glucopyranose Pentaacetate.—α-D,α-L-Glucose (0.200 g.) and 2 ml. of anhydrous pyridine were cooled to 0° and 1.4 ml. of acetic anhydride was added slowly under mechanical stirring while maintaining the same temperature. The suspension was stirred at 0° for twenty hours after which time the solution was poured slowly into 10 ml. of ice and water. The crystalline material was removed by filtration, washed with water and recrystallized from 95% ethanol; yield 0.258 g. (61%), m. p. 140–140.5°. The substance formed complex rhombic crystals.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.21; H, 5.75.

This product showed the same X-ray powder diffraction diagram (Table I) as that obtained by recrystallizing equal amounts (0.2000 g.) of the α-D and the below-described α-L-glucose pentaacetate from 95% ethanol; m. p. 141–141.5°, mixed melting point unchanged; m. p. 113–115° on admixture with the below-described β-D,β-L-pentaacetate of m. p. 125–126°.

α-L-Glucopyranose Pentaacetate.—α-L-Glucose[3] (0.40 g.) was acetylated as described above for the α-D,α-L isomer and the crude crystalline product (0.77 g., 89%, m. p. 108–110°) was recrystallized from ethanol-water; m. p. 112–113°, $[\alpha]^{25}\text{D}$ −101° (*c* 4.4, chloroform) in agreement (opposite sign) with those cited by Hudson and Dale[8] for α-D-glucose pentaacetate.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.29; H, 5.30.

β-L-Glucopyranose Pentaacetate.—α-L-Glucose[3] (0.20 g.) was heated on a steam-bath with freshly fused sodium acetate (0.12 g.) and acetic anhydride (2.0 ml.) and heating was maintained for two hours after solution, which required about thirty minutes. The crystalline material (0.38 g., 88%, m. p. 130–131°) obtained on pouring the reaction mixture into 20 ml. of ice and water, was recrystallized from 95% ethanol; m. p. 131–132°, $[\alpha]^{25}\text{D}$ −3.9° (*c* 2.9, chloroform) in agreement (opposite sign) with those cited by Hudson and Dale[8] for β-D-glucose pentaacetate.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.30; H, 5.32.

β-D,β-L-Glucopyranose Pentaacetate.—Equal amounts (0.1000 g.) of β-D- and β-L-glucose pentaacetate were recrystallized from 95% ethanol; m. p. 125–126°, needles.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.60; H, 5.43.

Summary

1. A crystalline form of racemic glucose has been prepared.

2. The crystalline pyranoid pentaacetates of α-L-, β-L-, α-D,α-L- and β-D,β-L-glucose are described.

3. X-Ray powder diffraction diagrams of the above compounds have been obtained.

4. Mild acetylation of the racemic glucose produces α-D,α-L-glucopyranose pentaacetate.

5. The D,L-glucose (m. p. 112–113.5°) described is a racemic mixture of the α-D and α-L forms of glucose, probably pyranoid.

6. The described pyranoid pentaacetates of α-D,α-L- and β-D,β-L-glucose are true racemic compounds.

COLUMBUS, OHIO RECEIVED APRIL 29, 1949

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(8) C. S. Hudson and J. K. Dale, THIS JOURNAL, **37**, 1264 (1915).

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Liquid–Vapor Equilibrium of Ethanol–Methylcyclohexane Solutions

BY CARL B. KRETSCHMER AND RICHARD WIEBE

In two recent publications results on the liquid–vapor equilibria of ethanol–isoöctane[2] and ethanol–toluene[3] solutions were described. The work has now been extended to solutions of ethanol in methylcyclohexane. The only previous measurements on this system are those of Isii,[4] who measured the total vapor pressure at 0 to 30°.

Experimental

The apparatus, method and purification of the ethanol have been described fully in previous articles.[2,3] A commercial grade of methylcyclohexane was fractionally distilled in an efficient column and percolated through a column of silica gel. Facilities for a determination of the freezing point were not available but the physical properties, d^{25}_4 0.76496, $n^{25}\text{D}$ 1.42059, are in satisfactory agreement with the values given by Forziati[5] for a sample containing 0.10 mole per cent. impurity, *viz.:* d^{25}_4 0.76501, $n^{25}\text{D}$ 1.42056.

Since the densities of the two liquids differ by only 0.02, solutions were analyzed by means of their refractive indices for the green mercury line (5461 Å.). A Bausch and Lomb precision refractometer was used. In order to establish the relation between composition and index of refraction, solutions were made up by weight as previously described.[2] Because of the theoretical and practical interest in the change of volume on mixing, the densities of these solutions were measured as well as their refractive indices. Table I gives the resulting values. The volume changes are all positive and are remarkably close to the values for

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) C. B. Kretschmer, J. Nowakowska and R. Wiebe, THIS JOURNAL, **70**, 1785 (1948).

(3) C. B. Kretschmer and R. Wiebe, *ibid.*, **71**, 1793 (1949).

(4) N. Isii, *J. Soc. Chem. Ind. Japan*, **38**, Sup. Binding, 659 (1935).

(5) A. F. Forziati, A. R. Glasgow, C. B. Willingham and F. D. Rossini, *J. Res. Nat. Bur. Standards*, **36**, 129 (1946).

ethanol–isoöctane solutions at the same temperature. Compositions of the liquid and vapor samples were calculated from their indices of refraction with the aid of the indices listed in Table I. The accuracy of such analyses is believed to be about 0.1 unit in the percentage by weight.

TABLE I

DENSITIES AND REFRACTIVE INDICES OF ETHANOL–METHYLCYCLOHEXANE SOLUTIONS AT 25°

Ethanol Wt. fract.	Mole fract.	n^{25}_{5461}	d^{25}_{4}	$10^6\ \Delta v$, ml./g.
0.0000	0.0000	1.42240	0.76496	0
.0327	.0671	1.41987	.76457	176
.0882	.1709	1.41605	.76484	316
.1586	.2866	1.41133	.76562	418
.3366	.5196	1.40002	.76836	547
.5376	.7125	1.38755	.77226	562
.5639	.7337	1.38600	.77284	553
.5662	.7356	1.38587	.77288	554
.6610	.8060	1.38021	.77508	504
.8018	.8961	1.37195	.77877	364
.8518	.9245	1.36904	.78024	290
1.0000	1.0000	1.36073	.78505	0

The results of the liquid–vapor equilibrium measurements at 35 and 55° are given in Table II. The vapor pressures for pure ethanol were taken from our previous work[3]; those for methylcyclohexane were calculated from the equation published by Willingham and co-workers.[6] Since the vapor pressure curves for this system are similar to those for the other systems studied, they are not reproduced here.

TABLE II

LIQUID–VAPOR EQUILIBRIUM OF ETHANOL–METHYLCYCLOHEXANE SOLUTIONS AT 35 AND 55°

Mole fract. ethanol Liquid, x	Vapor, y	p, mm.	Δy^a	Log γ_1	Log γ_2
		35°			
0.0000	0.0000	73.62	......	....	0.0000
.0526	.4645	135.40	0.0027	1.0634	.0120
.1446	.5118	146.97	−.0008	0.7016	.0509
.2878	.5362	151.27	.0024	.4353	.1204
.4052	.5471	152.36	.0018	.2986	.1913
.5403	.5575	152.93	−.0025	.1834	.2947
.6914	.5817	152.22	−.0042	.0927	.4414
.8450	.6423	145.73	−.0042	.0299	.6541
.9676	.8369	120.04	.0048	.0024	.9106
1.0000	1.0000	103.14	......	.0000	....
		55°			
0.0000	0.0000	168.10	......	....	0.0000
.0528	.4835	319.83	0.0012	1.0189	.0072
.1251	.5375	352.80	−.0026	0.7322	.0345
.2205	.5645	368.00	.0008	.5255	.0758
.3621	.5846	376.34	.0028	.3347	.1517
.5071	.5988	379.83	.0009	.2028	.2524
.6832	.6244	380.06	−.0024	.0918	.4160
.7792	.6528	375.78	−.0027	.0492	.5340
.9347	.7879	337.52	.0038	.0060	.8046
1.0000	1.0000	279.89	......	.0000	....

[a] Observed values minus those calculated from equation (1).

Discussion

The vapor compositions were fitted by the empirical equation previously used[3]

$$y(1-x)/[x(1-y)] = \alpha = (A - Bx)/[(x + C)(1 - 2C + Cx)] \quad (1)$$

where x and y are the mole fractions of ethanol in liquid and vapor, respectively. The following values of the constants were found to represent the data for ethanol–methylcyclohexane solutions: at 35°, $A = 1.131$, $B = 1.003$, $C = 0.020$; at 55°, $A = 1.339$, $B = 1.179$, $C = 0.028$. That the fit is satisfactory is shown by the deviations listed in Table II. Fig. 1 illustrates the method of fitting this equation. The quantity $q = \alpha(x + C)(1 - 2C + Cx)$ is plotted against x for various values of C, and that value of C is chosen which makes the points lie closest to a straight line, bearing in mind that the points must be given weights proportional to $y(1 - y)/q$ if all the values of y are assumed equally accurate.

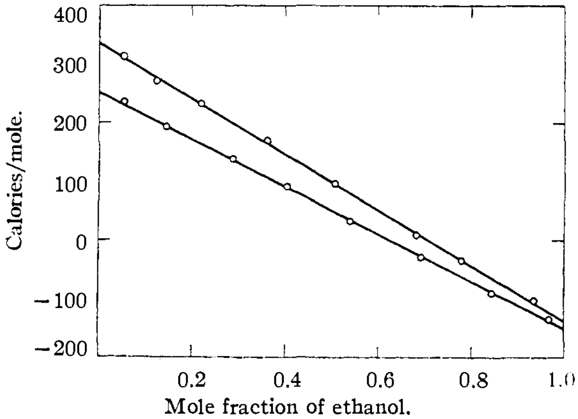

Fig. 1.—Relative volatilities of ethanol–methylcyclohexane solutions: upper curve, 55°, $C = 0.028$; lower curve, 35°, $C = 0.020$.

Equation (1) was substituted into the Gibbs–Duhem relation in the form given as equation (3) of our previous paper,[3] and used to calculate the vapor pressure at mole fractions of 0.5 and 1, for both temperatures. The liquid molal volumes and second virial coefficients for ethanol were the same as used previously.[3] For methylcyclohexane, the critical constants given by Kay,[7] were used with the equation of state of Keyes, Smith and Gerry in the form used by Scatchard and Raymond,[8] to give the following values of the second virial coefficient: at 35°, −3361; at 55°, −2592 cc./mole. Liquid molal volumes were calculated from the density equation of Massart.[9] The calculated vapor pressures differ from observed values by

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(6) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Res. Nat. Bur. Standards*, **35**, 219 (1945).

(7) W. B. Kay, THIS JOURNAL, **69**, 1273 (1947).

(8) G. Scatchard and C. L. Raymond, *ibid*, **60**, 1278 (1938).

(9) L. Massart, *Bull. soc. chim. Belg.*, **45**, 76 (1936).

0.8% or less. This result may be taken to indicate a satisfactory degree of thermodynamic consistency in our data.

Redlich and Kister[10] have developed the following equation to represent the behavior of solutions containing an associating component such as an alcohol.

$$\log(\gamma_1/\gamma_2) = A'(K,x) + B'(1 - 2x) + C'[6x(1 - x) - 1] \quad (2)$$

Here γ_1 and γ_2 are the activity coefficients of alcohol and hydrocarbon, respectively. We have used primes to distinguish the notation from that of equation (1). A' is a function of x and of K, the equilibrium constant for the association reaction $\mathrm{ROH} + (\mathrm{ROH})_n \rightleftarrows (\mathrm{ROH})_{n+1}$. The form of the function $A'(K,x)$ is given in reference (10b), equation (20). In equation (2) above, the terms in A' and B' are odd functions of $(1 - 2x)$, while the term in C' is, of course, an even function.

To test the applicability of equation (2) to the present data, the values of $\log \gamma_1$ and $\log \gamma_2$ listed in Table II were calculated from the experimental data by use of the relation

$$\log \gamma_1 = \log(y_1 p/x_1 p_1) + (1/2.303RT)(\beta_1 - v_1)(p - p_1) \quad (3)$$

Here x_i and y_i are the mole fractions of component i in liquid and vapor; p_i, β_i and v_i are the vapor pressure, second virial coefficient, and liquid molal volume of component i, and p is the vapor pressure of the solution. Values of $\log(\gamma_1/\gamma_2)$ were plotted against x, and the resulting curve was resolved into odd and even functions of $(1 - 2x)$ by means of the relation

$$f(x) = {}^1/_2[f(x) - f(1 - x)] + {}^1/_2[f(x) + f(1 - x)] \quad (4)$$

It was found that the odd function could be represented quite accurately by the odd terms of equation (2). However, the even function is represented poorly by the term $C'[6x(1 - x) - 1]$. This is shown in Fig. 2, where the plotted points have been taken from the experimental curve of $\log(\gamma_1/\gamma_2)$ vs. x, and the curve is calculated for $C' = -0.111$. The deviations represent errors in y of up to 0.015 mole fraction. The following values of the parameters were found for ethanol–methylcyclohexane solutions: at 35°, $K = 16$, $B' = 1.350$, $C' = -0.111$; at 55°, $K = 16$, $B' = 1.331$, $C' = -0.111$. The ethanol–toluene system[3] at 35° can be represented by $K = 6$, $B' = 0.994$, $C' = -0.130$, with deviations very similar to those shown in Fig. 2. The above values of K are anomalous in that one would reasonably expect K to decrease appreciably between 35 and 55°. Furthermore, the theory behind equation (2) requires that K have the same value for solutions of the same alcohol in different hydrocarbons at the same temperature. However, it has been emphasized[10] that K is very sensitive to experimental errors, and also, we might add, to deviations from the simplifying assumptions necessarily introduced in deriving equation (2).

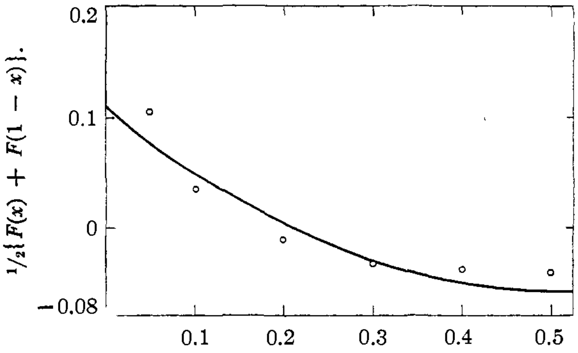

Fig. 2.—Ethanol-methylcyclohexane solutions at 55°: points, even component of $\log(\gamma_1/\gamma_2)$; curve, $0.111[1 - 6x(1 - x)]$.

TABLE III

EXCESS THERMODYNAMIC FUNCTIONS OF ETHANOL–METHYLCYCLOHEXANE SOLUTIONS IN CALORIES/MOLE

Mole fract. ethanol	G^E, 35°	G^E, 55°	TS^E, 35°	H^M_-
0.0528	95	91	79	174
.1251	186	183	42	228
.2205	263	263	− 9	254
.3621	323	327	−62	261
.5071	334	341	−92	242
.6832	287	292	−95	192
.7792	231	235	−79	152
.9347	86	87	−29	57

The excess thermodynamic functions in Table III and Fig. 3 were calculated from the experimental values of y and p by the usual method.[3] The behavior is similar to that of the ethanol–toluene system, as well as various systems containing methanol which have been studied and discussed by Scatchard and co-workers.[11] Little

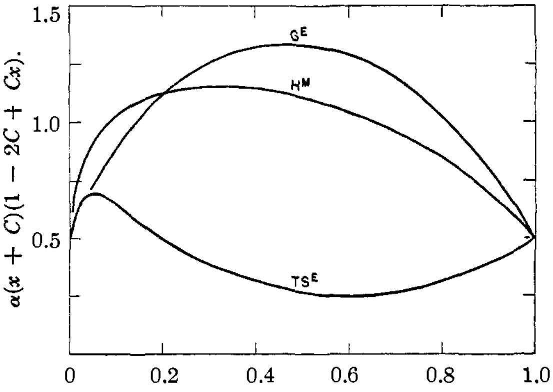

Fig. 3.—Excess thermodynamic functions of ethanol-methylcyclohexane solutions at 35°.

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[10] (a) O. Redlich and A. T. Kister, *J. Chem. Phys.*, **15**, 849 (1947); (b) *Ind. Eng. Chem.*, **40**, 345 (1948).

[11] G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **68**, 1957, 1960 (1946); S. E. Wood, *ibid.*, **68**, 1963 (1946); *J. Chem. Phys.*, **15**, 358 (1947).

can be added to their discussion except to say that a completely satisfying theory of the behavior of such solutions is not yet possible, and to emphasize again the fact that interactions between the unlike molecules are involved, in addition to the type of association of the alcohol postulated by Redlich and Kister.[10]

Summary

For the system ethanol–methylcyclohexane, densities and refractive indices have been measured at 25°. Total and partial vapor pressures have been determined at 35 and 55°. Thermodynamic consistency of the data was found to be satisfactory.

Vapor compositions are represented by the empirical equation previously developed by the authors, to within 0.005 mole fraction. They can be represented by an equation developed by Redlich and Kister, with somewhat less accuracy, and with rather anomalous values of the equilibrium constant involved.

The excess free energy, entropy and enthalpy have been calculated from the data, and exhibit a similar behavior to that of other alcohol–hydrocarbon systems.

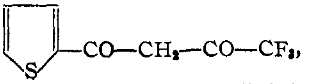
PEORIA 5, ILLINOIS RECEIVED MARCH 24, 1949

[CONTRIBUTION FROM THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Fractional Separation of Zirconium and Hafnium by Extraction with Thenoyltrifluoroacetone[1]

BY E. H. HUFFMAN AND L. J. BEAUFAIT

The synthesis of thenoyltrifluoroacetone,



$—CO—CH_2—CO—CF_3$, has recently been reported by Reid and Calvin[2] and a study of the extraction of its zirconium chelate into benzene has been reported by Connick and McVey.[3] The work reported in this paper on the separation of zirconium and hafnium by means of this β-diketone was undertaken at the suggestion of M. Calvin and G. T. Seaborg. A study has been made of some differences in the extractions of zirconium and hafnium by benzene solutions of thenoyltrifluoroacetone (referred to as HT in equations and tables) from aqueous 2 *M* perchloric acid and the results applied to separations of these elements.

Zirconium is generally regarded as being in the form of ZrO^{++} in acid solutions. The complexing of zirconium by the diketone is negligible in the aqueous phase and the only important species in the benzene phase is ZrT_4.[3] The reaction then is expressed by the equation

$$ZrO^{+2} + 4HT = ZrT_4 + H_2O + 2H^+$$

and, assuming constant acid concentration, the equilibrium constant by

$$\log K = \log [ZrT_4]/[ZrO^{+2}] - 4 \log [HT] = \log R - 4 \log [HT]$$

where *R* is the extraction coefficient. If the zirconium is in the form of the simple Zr^{+4} ion in 2 *M* perchloric acid, as recently reported,[4] the expression for the equilibrium constant is not changed, providing that the zirconium ion is monomeric. Values for *R* and *K* have previously been determined[3] for zirconium using trace amounts of radioactive Zr^{95}.

The close similarity of zirconium and hafnium in chemical behavior makes it logical to assume that the above equations apply to both elements. The determination of values for *R* and *K* for both zirconium and hafnium, using macro quantities and concentrations for which the zirconium ions has been shown to be a monomer in 2.0 *M* perchloric acid,[4] has been carried out in this work in the thenoyltrifluoroacetone concentration range of 4×10^{-3} to 3×10^{-2} for zirconium and 10^{-2} to 7×10^{-2} for hafnium.

Experimental

Materials.—Thenoyltrifluoroacetone of 99.5% purity was obtained from M. W. Davis and H. R. Lehman of this Laboratory. Weighed amounts were dissolved in reagent thiophene-free benzene to give solutions of the desired concentrations.

Zirconium solutions were prepared in a manner similar to that of Connick and McVey.[3] Recrystallized $ZrOCl_2 \cdot 8H_2O$ was dissolved in 2.0 *M* perchloric acid to prepare a stock solution of approximately 0.09 *M* zirconium.

Tracer zirconium solutions were prepared from carrier-free Zr^{95} in 5% oxalic acid which was received from the Isotopes Branch, United States Atomic Energy Commission. This solution was made about 10 *M* in nitric acid and carrier zirconium added from the above stock solution. The solution was purified by the following treatment.[3] A small amount of 0.1 *N* potassium permanganate was added to precipitate manganese dioxide which carries the radioactive columbium but not zirconium. This precipitation was carried out three times to remove both oxalic acid and columbium. The zirconium solution was then diluted to about 1 *M* nitric acid and extracted with 0.02 *M* thenoyltrifluoroacetone in benzene, and the benzene phase washed twice with 2 *M* perchloric acid. The benzene solution was removed to a platinum dish and fumed with sulfuric acid with the addition of small amounts of 30% hydrogen peroxide to destroy organic matter. It was then diluted and zirconium hydroxide precipitated with ammonium hydroxide. The precipitate was dissolved in hydrochloric acid and the

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[1] This paper is based on work done under the auspices of the Atomic Energy Commission.

[2] J. C. Reid and M. Calvin, MDDC-1405(BC-75), August 13, 1947.

[3] R. E. Connick and W. H. McVey, The Aqueous Chemistry of Zirconium, UCRL-101, March 1, 1948.

[4] W. H. Reas, Thesis, University of California, 1948.