The observed moments agree with those calculated on the assumption that each substance contains a ferro- or cobalticyanide ion in which the transition element is forming d^2sp^3 bonds[6] to the cyanides; the other heavy metals exist as simple ions. The experimental values are also in accord with previous observations of the magnetic moments of these ions; manganese, nickel, and copper have very little orbital moment, while that of cobalt is nearly unquenched.[7] The magnetic moments calculated on the basis of any other structural formulas than the one suggested here are incompatible with the experiments. Calculations were made for each compound using the four structural formulas that would permit all possible combinations of ionic and d^2sp^3 bonds. Allowance was made for the moments arising from spin alone and also for maximum orbital contribution.

Acknowledgment.—The authors wish to thank Professor Linus Pauling of the California Institute of Technology for his interest in the progress of the investigation and for his criticism during the writing of this paper.

Summary

The compounds $K_2MnFe(CN)_6$, $K_2CoFe(CN)_6$, $K_2CuFe(CN)_6$, $KCoCo(CN)_6$, $KCoCo(CN)_6 \cdot 2H_2O$ and $KNiCo(CN)_6$ have been prepared and their magnetic susceptibilities measured. The results are in agreement with the assumption that covalently bonded ferrocyanide or cobalticyanide ions are present in the compounds containing ferrous or cobaltic ions, respectively. All other heavy metals are present as simple ions.

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[6] Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[7] See J. H. van Vleck's discussion, "The Theory of Electric and Magnetic Susceptibilities," Oxford at the Clarendon Press.

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

The System Ethyl Alcohol–Glycerol–Benzene at 25°

BY HUGH J. MCDONALD

A review of the literature showed that no data had been collected on the solubility relationships of the system, ethyl alcohol–glycerol–benzene. The distillation of such a ternary solution, with the determination of liquid–vapor composition data, should be interesting. There has been evident, also, during the last few years, considerable interest in the problem of the separation of the pure components from mixtures of glycerol and ethyl alcohol but very little work has been done on the effect of a third component on their mutual solubility. As a preliminary step in the study of the system, it was thought advisable to determine the region of immiscibility and the tie line relationships.

Materials.—Thiophene-free benzene, the best grade obtainable from Eastman Kodak Company, was used without further purification.

Ethyl alcohol (95%) was kept for a week in contact with dried calcium oxide and shaken from time to time, then distilled. The process was repeated, when the alcohol distilled, using a long fractionating column, within three-tenths of a degree; the middle portion was used.

Glycerol of C. P. grade was purified by repeated distillation under reduced pressure.

Procedure and Results.—The titrations involved in determining the curve bounding the region of immiscibility were carried out at 25.00 ± 0.05° in small glass-stoppered bottles, which were shaken in the constant temperature bath. Preliminary titrations were made and the curve sketched in, so that in the final titrations dropwise addition of alcohol was required over only a small range.

The end-points, it was found, were most accurately determined by adding the ethyl alcohol to the benzene–glycerol mixture until the cloudiness just disappeared, rather than trying to observe the first appearance of cloudiness on adding benzene to the ethyl alcohol–glycerol mixtures. The disappearance of cloudiness was observed by looking through the solution at a light bulb behind the all-glass water-bath.

It had been hoped that measurements of the refractive indices along the immiscibility curve would serve to determine the distribution of ethyl alcohol between glycerol and benzene. It was found, however, that the refractive indices changed only a little in the third decimal place all along the top of the curve. Surface-tension measurements were attempted, using a Du Nouy tensiometer, but they were not easily reproducible due to the rapid, uneven, evaporation of benzene and ethyl alcohol from the exposed surfaces of the solution. Density measurements using a pycnometer were also difficult to reproduce, due to the high viscosity of some of the solutions. Finally a modified form of a viscosimeter was found to yield values which were quite reproducible and of as good an order of accuracy as needed.

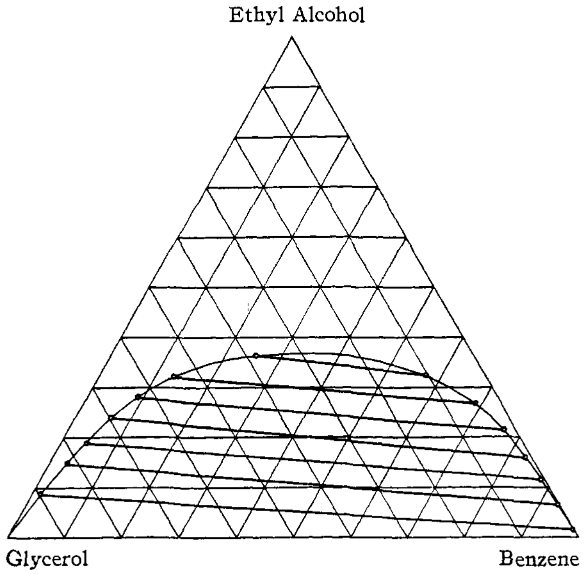

Fig. 1.—The system ethyl alcohol–glycerol–benzene at 25°.

The apparatus consisted of a 10 cc. narrow-bore pipet, graduated along its entire length into tenths of a cubic centimeter. This was inserted through a two-hole rubber stopper up to the 0.1 cc. mark, the other hole of the stopper having in it a short length of glass tubing. The stopper, with pipet and air-vent tube, was inserted into a 100 cc. test-tube. The liquid under investigation was poured into the bottom of the tube so as to just reach the 10 cc. mark on the pipet when the stopper through which it passed was inserted into the test-tube. The liquid was drawn up by suction above the zero mark of the pipet, and the time required for the meniscus to drop from the zero to the 8 cc. mark was determined with a stop watch.

The apparatus was calibrated by making up a series of solutions along the immiscibility curve and determining the time of fall for each. All measurements were made at 25.0°, the tube being immersed in the constant temperature-bath. When the time in seconds was plotted against the per cent. by weight of benzene and of glycerol in the solutions, two smooth curves resulted. It was then necessary merely to determine the time of fall of a given solution along the miscibility curve, in order to determine its composition by weight. A solution containing 25.0% glycerol and 38.0% benzene would fall in 10.5 seconds, while one containing 65.0% glycerol and 8.0% benzene would fall in 46.0 seconds.

The tie lines were determined by making up several samples of alcohol, glycerol and benzene having compositions within the immiscibility region, and allowing them to stand twenty-four hours in sealed separatory funnels immersed in the water-bath at 25.0°. The mixtures separated into an upper and a lower layer which were easily divided by the use of the separatory funnel. The modified viscosity measurements were made on each layer and the compositions of the samples determined from the graphs mentioned above.

The weight per cents. of alcohol and of glycerol are collected in Table I and plotted in Fig. 1. In Table II are listed the compositions of conjugate solutions.

TABLE I

SOLUBILITIES AT 25.0°

Weight % glycerol	Weight % benzene	Weight % glycerol	Weight % benzene
89.6	1.4	29.8	33.3
82.5	3.0	26.0	37.1
76.5	4.5	21.8	41.8
68.1	6.9	17.5	46.9
62.2	9.3	12.4	54.0
55.1	12.9	8.7	60.0
48.7	17.1	6.4	64.1
42.0	22.3	4.0	69.8
35.3	27.8	2.3	75.8
34.2	23.8	1.1	82.7
31.5	31.5		

TABLE II

COMPOSITIONS OF CONJUGATE SOLUTIONS AT 25.0°

Lower layer, weight %		Upper layer, weight %	
Glycerol	Benzene	Alcohol	Benzene
89.8	1.4	1.4	98.4
81.9	3.2	6.3	93.4
76.5	4.4	10.4	84.0
69.7	6.3	16.1	82.8
62.9	9.0	21.7	76.1
54.6	13.4	26.8	68.6
38.7	25.0	32.3	57.3

Grateful acknowledgment is made of the assistance given by Mr. Ralph Petri in much of the laboratory work.

Summary

The solubility relationships, region of immiscibility, and tie lines for the ternary system ethyl alcohol–glycerol–benzene have been determined at 25.0°.

A modified viscosity determination was devised to analyze the composition of the conjugate solutions, when measurements of refractive index, surface tension and density proved to be unsatisfactory.

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