able suggestions and criticism in preparing this manuscript, and to Dr. H. Gruber for supplying some of the biological fluids tested.

Summary

The surface tension of small amounts of liquid is determined by the height attained in a calibrated tube consisting of a narrow capillary fused to a wider one. This method is as accurate as, and subject to most of the limitations of, the usual capillary rise method.

BROOKLYN, N. Y. RECEIVED APRIL 22, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Cryoscopic Investigation of Anomalies in the Behavior of Ethylene Chloride

BY HUGO HUETTIG, JR., AND CHARLES P. SMYTH

The abnormally high value found for the dipole moment of ethylene chloride in benzene as compared to its value in other solvents has been attributed to the presence of a very strong field of force immediately surrounding the benzene molecule or to the actual linking of the solute and solvent molecules to form a complex.[1,2,3,4,5,6] Anomalous dispersion found in solutions of ethylene chloride in ether at low temperatures was regarded as indicating the formation of an intermolecular compound of ethylene chloride and ether, which received support from the high apparent moment calculated for ethylene chloride with an equimolecular quantity of ether in solution in carbon tetrachloride.[5] In view of the importance of ethylene chloride as providing a means of studying intramolecular potential energy, it has seemed of interest to investigate these solutions by freezing point determinations.

Purification of Materials

Ethylene Chloride.—Material from the Eastman Kodak Company was washed with very dilute sodium hydroxide, dried over calcium chloride and fractionally distilled; b. p. 83.5°.

Benzene.—Thiophene-free material was washed with concentrated sulfuric acid, dried over sodium and fractionally distilled; b. p. 80.2°.

Ethyl Ether.—U. S. P. grade material was treated with acid permanganate solution, washed with sodium hydroxide in a saturated sodium chloride solution, dried over calcium chloride and fractionally distilled; b, p. 35.1°.

Experimental Procedure

The freezing points of the solutions were measured in a Pyrex tube 30 cm. long and 2.2 cm. in diameter fitted with a stirrer and surrounded by an air jacket formed by a second tube 3.2 cm. in diameter, which dipped into a Dewar tube containing, in the case of the benzene solutions, an acetone–carbon dioxide slush and, for the ether solu-

TABLE I

FREEZING POINT DATA

Mol. % ethylene chloride	Freezing point, °K.	Eutectic arrest, °K.
Ethylene Chloride–Benzene		
0.0	278.5	
10.3	271.2	
17.2	266.2	
27.4	258.3	218.9
39.8	247.6	
50.8	236.5	
61.7	223.9	
67.3	218.9	218.9
77.6	224.5	
89.5	232.0	218.9
100.0	237.3	
Ethylene Chloride–Ethyl Ether		
0.0	149.9	
	156.9	
2.0	149.3	149.1
3.0	149.1	149.1
4.7	149.9	149.1
	151.7	149.1
6.1	151.6	149.0
	155.6	149.0
9.7	154.7	
	161.0	
11.4	157.9	149.1
	162.8	149.1
13.4	164.2	
16.4	166.9	149.2
21.5	168.5	149.0
25.0	169.4	169.4
29.3	173.3	169.3
31.8	178.2	169.5
32.8	180.9	
47.2	200.2	
65.4	217.9	
76.6	224.4	
90.6	232.2	
100.0	237.3	

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[1] Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).

[2] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

[3] Van Arkel and Snoek, *Z. physik. Chem.*, **B18**, 159 (1932).

[4] Müller, *Physik. Z.*, **34**, 689 (1933).

[5] Stearn and Smyth, THIS JOURNAL, **56**, 1667 (1934).

[6] Mizushima and Higasi, *Proc. Imp. Acad.* (Japan), **8**, 482 (1932).

tions, liquid air. The rate of cooling was controlled by varying the amount of carbon dioxide in the slush or raising the freezing point tube to different heights above the liquid air. The temperatures were read with a Mueller bridge and a three-lead platinum resistance thermometer, the bulb of which was well immersed in the solution to be measured. Several runs were made on each solution to check the freezing point and a possible secondary arrest, the probable error being about 0.2°. The freezing point-composition diagrams were obtained for the two systems ethylene chloride–benzene and ethylene chloride–ether.

Experimental Results

Table I gives the molecular percentage of ethylene chloride in each mixture in the first column, the absolute temperature of the freezing point in the second column, and the temperature of the eutectic arrest, when noted, in the third column. The absence of a temperature reading in this column may merely indicate that no observation of it was made. In the ethylene chloride–ether system, the freezing point of a metastable form was sometimes observed, but the freezing point of the stable form could always be detected by melting and freezing the mixture again. For such cases, two freezing points are given in Table I, the lower being that of the metastable form. The resulting equilibrium diagrams for the two systems are shown in Figs. 1 and 2.

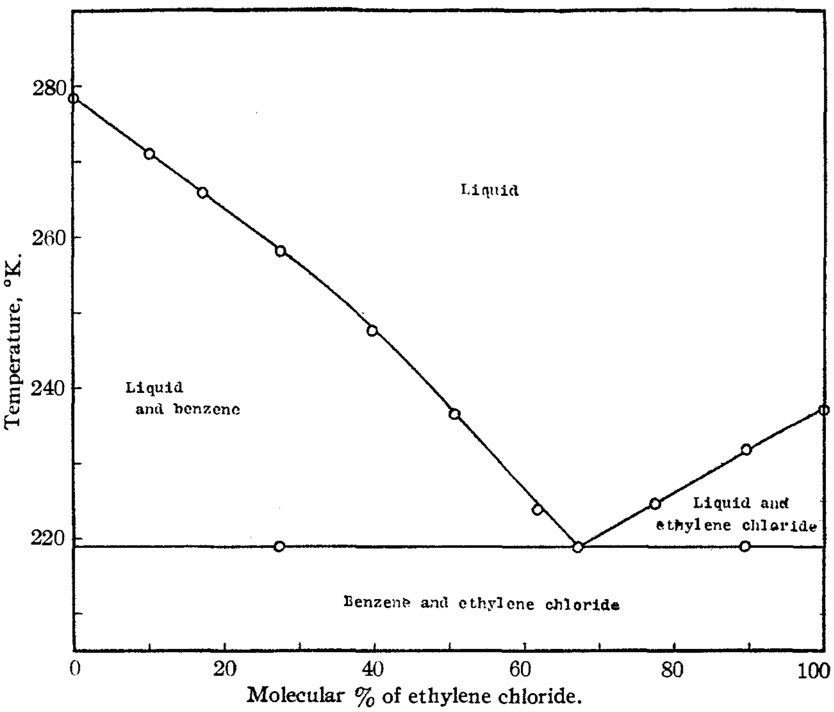

Fig. 1.—Ethylene chloride–benzene system.

Discussion of Results

The simple diagram for the ethylene chloride–benzene system in Fig. 1 gives no evidence of any compound formation, not the slightest discontinuity appearing in the curves between the freezing points of the pure liquids and the eutectic point. If the usual molal freezing point depression constant 5.12° is used for benzene, the theoretical depression may be calculated for the dilute solutions of ethylene chloride in benzene. Extension of the calculation to a solution as concentrated as that containing 10% ethylene chloride gives a theoretical depression of 7.3° as compared to a value 7.1° read from the curve in Fig. 1, while compound formation between solute and solvent should, of course, tend to make the observed depression abnormal. This failure to detect compound formation confirms that of Harada, who is reported in a paper published[7] while this investigation was being carried out as finding a normal molecular weight for ethylene chloride by cryoscopic measurement with benzene as solvent. As opposed to the indications given by freezing point measurements, Kubo[8] has recently explained his polarization values quantitatively by the assumption of a one-to-one compound of ethylene chloride and benzene. This is evidence essentially similar to that which led Stearn and Smyth[5] to the supposition of a loose complex.

The equilibrium diagram for the ethylene chloride–ether system in Fig. 2 is much less simple. Each of the two freezing points obtained for ether is but 0.1° higher than that given in "International Critical Tables." A eutectic point lies only 0.8° below the lower freezing point, that of the β form. For ethylene chloride content just above 3%, the eutectic composition, two alternative freezing points were found, the upper and, presumably, stable series being indicated by sharper

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(7) Mizushima, Morino and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25**, 190 (1934).

(8) Kubo, *Bull. Inst. Phys. Chem. Research* (Tokyo), **13**, 1221 (1934).

arrests as the ethylene chloride content increased, while the arrests corresponding to the lower series represented by a dotted line became less pronounced and finally disappeared beyond the 11.4% mixture. Only the one eutectic arrest was found throughout this region. Although there are various possible explanations of this metastable curve, none is sufficiently satisfactory to warrant discussion.

The mixture containing 25% ethylene chloride freezes sharply and evidently consists of a compound at the temperature of freezing. However, dissociation of the compound makes the curve so flat in this region that the descent to a eutectic just beyond the point corresponding to the composition of the compound was not detected in these measurements although it should exist if the uppermost branch of the freezing point curve does not meet the next branch at or to the left of the compound composition. The secondary arrests observed in the next two mixtures to the right are, in fact, at the same temperature as the freezing point of the compound. The determination of these secondary arrests was omitted in the case of the mixtures richer in ethylene chloride.

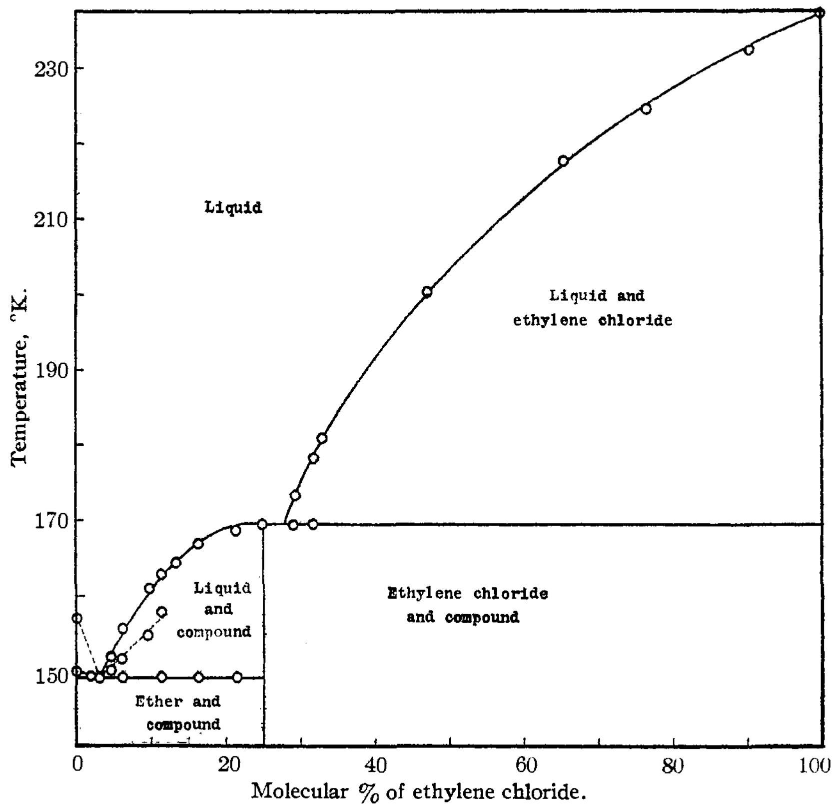

Fig. 2.—Ethylene chloride–ethyl ether system.

The formation of a compound of the formula $C_2H_4Cl_2 \cdot 3(C_2H_5)_2O$ is rather surprising if it is formed by linkage of oxygen and chlorine since one would expect one ether to be linked to each chlorine giving $C_2H_4Cl_2 \cdot 2(C_2H_5)_2O$ or possibly even two ethers to each chlorine giving $C_2H_4Cl_2 \cdot 4(C_2H_5)_2O$. The stability of the observed compound, however, suggests that the hypothetical compound $C_2H_4Cl_2 \cdot 2(C_2H_5)_2O$, which would presumably have a higher freezing point, would be too far dissociated to be detectable by the freezing point curve. Steric effects might prevent the attachment of four ether molecules to one of ethylene chloride. If, in the compound indicated by the diagram, one ether molecule were attached to each chlorine and the third had its oxygen linked to each of the two chlorines, the complex would be accounted for by the formation of a twelve-electron shell around each chlorine. Resort may also be had to the formation of hydrogen links to hold the complex together. In view of the fact, however, that our real knowledge of the nature of such intermolecular linkages seems to be epitomized by the dotted line mode of representation, it may be best to refrain from speculation.

In conclusion, it may be stated that, while freezing point investigations give no support to the hypothesis of a compound formation between ethylene chloride and benzene, they do not necessitate the abandonment of the idea of a possible loose complex of molecules of the two, which seems to offer an explanation of the abnormally high moment found for ethylene chloride in benzene as well as of the relative intensities of certain lines in its Raman spectrum in benzene solution.[7] The much more definite indications of complex formation given by dielectric constant measurements of ethylene chloride solutions in ether[5] are borne out by the indication of the somewhat unstable compound in Fig. 2.

The writers wish to express their indebtedness to Professor D. P. Smith for his kindness in discussing these results.

Summary

Freezing point measurements have been made in order to investigate the possibility of intermolecular compound formation in solutions of ethylene chloride in benzene and in ether. The equilibrium diagrams which have been constructed for the two systems give no sign of compound formation in the ethylene chloride–benzene system, but indicate the formation of an unstable compound $C_2H_4Cl_2 \cdot 3(C_2H_5)_2O$.

PRINCETON, NEW JERSEY RECEIVED JUNE 3, 1935

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Normal Potential of the Silver–Silver Iodide Electrode from 5 to 40°

BY BENTON BROOKS OWEN

The discordance between the recorded values of the normal potential of the silver–silver iodide electrode appears to be due to incomplete knowledge of the activity coefficient of hydriodic acid and the instability of its solutions, rather than to some uncertainty in the thermodynamic behavior of silver iodide. Various investigators[1] attest the stability and reproducibility of the electrode itself, and the general trustworthiness of measurements made with it in neutral solutions[1a,b] has recently been established[2] by the isopiestic method of comparing the activity coefficients of potassium chloride and iodide. Preliminary measurements[3] indicated that these electrodes behave normally in alkaline buffer solutions also. In the present research the normal potentials of two convenient types have been determined by comparing the silver iodide and silver chloride electrodes in borax solutions containing the corresponding halide. The method should be applicable to the study of other electrodes for which the determination of normal potentials by direct extrapolation is impracticable.

Discussion of the Method

The cells employed are of the type

$$H_2 \mid HBO_2(m_1),\ NaBO_2(m_2),\ KX(m) \mid AgX,\ Ag$$

in which X represents either iodide or chloride. The required normal potential can be conveniently expressed in terms of the potential of the cell (E_{KX}), the buffer ratio ($\rho = m_{HBO_2}/m_{BO_2^-}$), and the ionization constant (K) of boric acid[4] by the equation

$$E^0_{HX} - f(\gamma) = E_{KX} + k \log m + k \log \rho + k \log K \quad (1)$$

in which $f(\gamma)$ has been written for $k \log (\gamma_{Cl^-}\gamma_{HBO_2}/\gamma_{BO_2^-})$, and k for 0.00019844 T. Since $f(\gamma)$ vanishes for $\mu = 0$, E^0_{HX} can be determined by extrapolation of measurements on solutions obtained by successive dilutions of a suitable stock solution. This procedure was used to evaluate E^0_{HI} at 25°,[3] but was subsequently abandoned in favor of a less laborious method based upon the experimental fact[5] that $f(\gamma)$ is only 0.01 m. v. in borate buffers when $\rho \approx 1$, and $\mu \approx 0.01$. Furthermore, $f(\gamma)$ is practically uninfluenced by the substitution of similar ions (Na^+ for K^+) at the concentrations studied.[5] Accordingly, by writing equation (1) for both KI and KCl we obtain

$$E^0_{HI} = E^0_{HCl} + E_{KI} - E_{KCl} + k \log \frac{m_{KI}}{m_{KCl}} + k \log \frac{\rho_{KI}}{\rho_{KCl}} \quad (2)$$

Upon imposing the additional experimental condition that $m_1 = m_2 \approx m \approx 0.005$ in both solutions,[6] the last term may be neglected. In practice it is convenient to make up solutions approximating the above condition, and to adjust the observed potentials to correspond exactly to $m_1 = m_2 = m = 0.005$ by the equation

$$E^{0.005}_{KX} = E_{KX} + k \log (m_{KX}/0.005) \quad (3)$$

Equation (2) may therefore be written

$$E^0_{HI} = E^0_{HCl} + E^{0.005}_{KI} - E^{0.005}_{KCl} \quad (4)$$

Materials and Technique

The purification of the borax and potassium chloride, the preparation and manipulation of solutions, and the preparation of the hydrogen and silver–silver chloride electrodes are described

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(1) (a) Gelbach, THIS JOURNAL, **55**, 4857 (1933); (b) Harned and Douglas, *ibid.*, **48**, 3095 (1926); (c) Pearce and Fortsch, *ibid.*, **45**, 2852 (1923); (d) Gerke, *ibid.*, **44**, 1684 (1922); (e) Noyes and Freed, *ibid.*, **42**, 476 (1920); (f) Taylor, *ibid.*, **38**, 2295 (1916); (g) Jones and Hartmann, *ibid.*, **37**, 752 (1915).

(2) Robinson, *ibid.*, **57**, 1161 (1935).

(3) Owen, *ibid.*, **56**, 2785 (1934).

(4) Owen, *ibid.*, **56**, 1695 (1934).

(5) *Cf.* uppermost curve in Fig. 1, Reference 4.

(6) Departures from this condition of ±10% would introduce an error of only 0.01 to 0.02 m.v.