Electrochemical Study of Ethylene Glycol-Acetic Acid System

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Introduction

The well known effect of certain hydroxy bearing compounds in increasing the acidity of aqueous solutions of boric acid pointed to a further exploration into the possibility of such and other similar effects of ethylene glycol on anhydrous acetic acid. Hence a systematic investigation of electrical conductance, volume contraction, viscosity, dielectric constant, and refractometric measurements has been made and reported herein.

Experimental Procedure

Purest Eastman Kodak ethylene glycol was dried over anhydrous sodium sulphate, decanted and fractionally distilled under reduced pressure and the middle fraction collected. Dielectric constant determinations showed the same value both for the original material and for the purified one. So further requirements of ethylene glycol were drawn from the Eastman Kodak supply. Purest Kahlbaum glacial acetic acid was used. Ethylene glycol and acetic acid were kept at 30°C in a thermostat for several hours and by pipetting out the required volumes of the two compounds totalling 50 cc. into 250 cc. glass stoppered pyrex bottles, different compositions of the mixtures differing by 10 per cent were made ranging from 10 to 90 per cent. Weight per cent or mole per cent composition could be computed by considering the density of the glycol (1.10800) and that of acetic acid (1.03777) and their respective molecular weights.

For measuring the dielectric constant "Dekameter type DKO3" of Wissenschaftlich-Technische Werkstatten was used at a fixed frequency of 1.8 MC/S controlling the temperature of the cell with Hoppler's ultra thermostat.

A platinized vertical cell with a cell constant value of 0.1845 was used for measuring conductance. Resistance of the solutions was measured with conductivity bridge type LBR of Wissenschaftlich-Technische Werkstatten, at 50 cycles per second (due to high resistance of the solutions). Temperature was controlled at 30 ± 0.05°C using Townson and Mercer's thermostat, S427. The same thermostat, provided with glass panels with suitable arrangements, was used for viscometric measurements, with an Ostwald viscometer. Hilger's Abbe refractometer with Hoppler's utlra thermostat was used for making refractometric measurements. pH measurements were attempted with a Cambridge pH meter using a glass electrode. But no steady reproducible pH values could be recorded. Also with quinhydrone electrode irreproducible values were obtained. Results are reported below.

The resistance of ethylene glycol could not be measured with the above set-up due to its very high value. Hence in reporting equivalent conductivity values no solvent correction could be applied.

Discussion

Acetic acid is known, from surface tension measurements[1,2], to exist as $(C_2H_4O_2)_2$ throughout the temperature range from 15 to 150°C. From the variation of the Ramsay-Shield's constants with temperature[3] and the dispersion and absorption of polyhydric alcohols in the Hertzian region[4] molecular associations are known to exist in ethylene glycol.

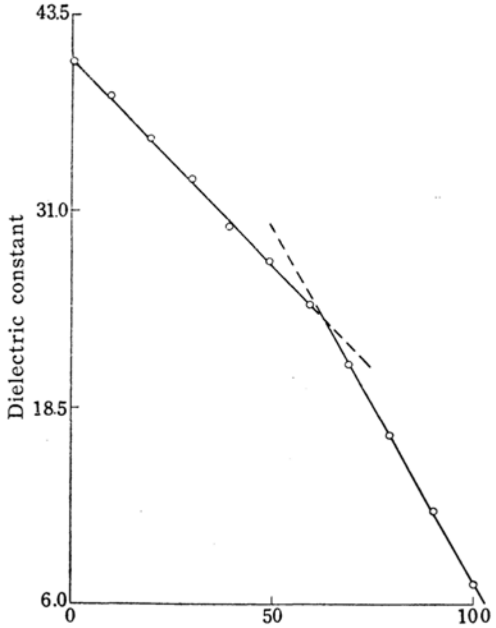

Fig. 1. Dielectric constant of ethylene-glycol-acetic acid system.

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[1] G. M. Bennet, *J. Chem. Soc.*, 351-360, 107 (1915).

[2] Emile Band, *Bull. Soc. Chim.*, 435-438, 13 (IV) (1913).

[3] G. G. Eliseef and W. A. Kurbastoff, *J. Russ. Phys. Chem. Soc.*, 1426-1427, 41 (1909).

[4] Pierre Girand and P. Abadie, *Compt. rend*, 1995-1997, 196 (1933)

TABLE I

ETHYLENE GLYCOL-ACETIC ACID SYSTEM

Vol. Percent of Acetic Acid (1)	Mole Percent of Acetic Acid (2)	Density (3)	Volume Contraction in c.c. (4)	Viscosity in Poises (5)	Dielectric Constant (6)	Molar Polarization (7)	Specific Conductivity (8)	Equivalent Conductivity (9)	Refractive Index (10)	Molar Refraction (11)
0	0	1.10800		0.1346	40.500	52.08			1.4270	14.38
10	9.712	1.10494	0.49	0.1188	38.250	51.83	6.151×10^{-6}	3.548×10^{-3}	1.4243	14.29
20	19.480	1.10086	0.67	0.1013	35.625	51.57	5.741×10^{-6}	1.651×10^{-3}	1.4198	14.18
30	29.350	1.09722	0.77	0.08750	33.000	51.23	6.331×10^{-6}	1.210×10^{-3}	1.4148	14.03
40	39.220	1.09224	0.71	0.07350	30.500	50.94	6.963×10^{-6}	0.9963×10^{-3}	1.4118	13.97
50	49.180	1.08798	0.71	0.06127	27.750	50.35	6.474×10^{-6}	0.7387×10^{-3}	1.4070	13.81
60	59.210	1.08130	0.56	0.04976	24.875	50.05	6.625×10^{-6}	0.6301×10^{-3}	1.4020	13.71
70	69.330	1.07477	0·48	0.03829	21.250	49.17	7.236×10^{-6}	0.5891×10^{-3}	1.3968	13.61
80	79.490	1.06583	0.32	0.02775	16.610	47.58	6.933×10^{-6}	0.4948×10^{-3}	1.3905	13.48
90	89.710	1.05539	0.17	0.01819	12.075	44.94	4.500×10^{-6}	0.2865×10^{-3}	1.3820	13.29
100	100.000	1.03777		0.01040	6.400	37.20			1.3700	13.09

A plot of dielectric constant values (column 6 of the Table) against mole per cent of acetic acid (Fig. 1) is made up of two straight lines intersecting at a composition of 62 mol. per cent of acetic acid. From 62 mol. per cent of acetic acid onwards the rate of fall of "D" is greater. All the mixtures have in each case a value for dielectric constant greater than to be expected if the variation is linear and at 62 mole per cent the deviation is a maximum. Likewise the plot of molar polarization against mole per cent of acetic acid (Fig. 2) is almost linear varying slightly with composition up to about 60 mole per cent of acetic acid, beyond which the fall is very rapid. All the mixtures have for each a value of molar polarization greater than to be expected if the variation is linear. The equation for molar polarization of a mixture

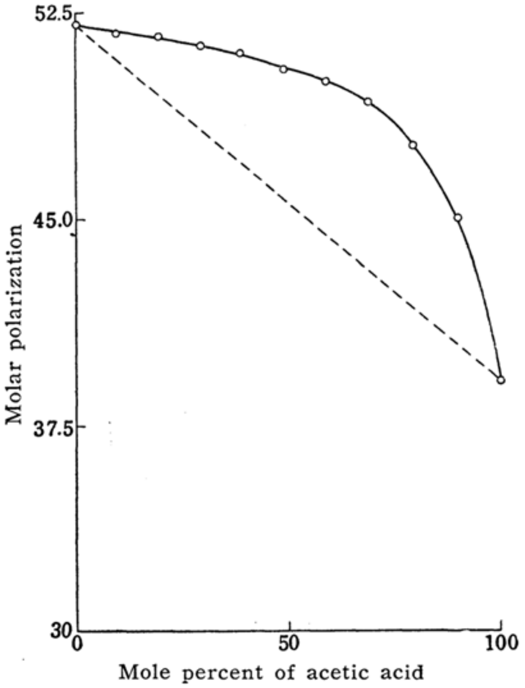

Fig. 2. Molar polarization of ethylene-glycol-acetic acid system.

$$P_{1,2}=\frac{D-1}{D+2}\cdot\frac{M_1x_1+M_2x_2}{\rho_{1,2}}$$

is expected to hold[5] only for solutions of non-associated liquids. But some workers[6] applied it with success to mixtures of associated liquids. It is known[7] that the effect of association on the dielectric constant depends on the sizes and shape of the participating dipoles. As a result of a greater electrostatic moment of a polymerised molecule[8] than the simple one the dielectric constant of the solvent will be greater in its associated state. De-association in some solutions is indicated by the lowering of the dielectric constant of that component in solution. Conversely when dipole-dipole interaction occurs the forces holding the electric charge will be weakened as a result of a probable increase of the electrostatic moment of the molecule and the dielectric constant of a component becomes greater in solutions than in pure state. It has been shown[9] that when liquids are mixed there are at least two simultaneous reactions taking place, a de-association of the liquids and a combination between the two liquids. These

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[5] G. Åkerlöf, *J. Am Chem. Soc.*, 4125, **54** (1932).

[6] W Graffunder and Erich Heymann, *Z. Physik. Chem.*, 744, 72 (1931).

[7] R. N. Kerr, *J. Chem. Soc.*, 2796-2804, 128 (1926).

[8] J. W. Williams and I. J. Krchma, *J. Am. Chem. Soc.*, 1886, 48 (1926).

[9] J. W. Williams and F. Daniels, ibid., 1490, 47 (1925).

factors should lead to opposing tendencies in any physical property. The only obvious conclusion is that starting from zero per cent ethylene glycol and proceeding towards per cent of it, the positive deviation of either the dielectric constant or the molecular polarization from linearity increases to a maximum at about 60 mole per cent of acetic acid and decreases from there onwards. It is probable that from zero to about 40 mole per cent of ethylene glycol dipole-dipole interaction predominates attaining its maximum at 40 mole per cent of ethylene glycol from where further increase of mole per cent of ethyleneglycol results in setting off a de-association of one or both of the components.

A plot of equivalent conductivity against mole per cent of acetic acid (Fig. 3) shows a rapid fall from 10 to 30 mole per cent of acetic acid, then a gradual fall up to about 60 mole percent round about which an inflexion occurs in the curve followed by a rapid fall towards the end. An electrochemical study of water-glycerol and water-ethylene glycol mixtures[10] showed that while it is possible to assume with ethanol the production of $EtOH_2^+$ ions, in the case of glycol or glycerol, ions of this type are formed to such a slight degree that the electrode potential remains practically unchanged. Since the equivalent conductivity, though slight, rises rapidly from 30 mole per cent of acetic acid downwards, it may be probable that in this region acetic acid starts slightly dissociating. From 60 mole per cent to 30 mole per cent the equivalent conductivity rises more rapidly than from 90 to 60 mole per cent of acetic acid, the overall increase in the former region being about double that in the latter. Hence it is probable that to anhydrous acetic acid, as more and more ethylene glycol is added, dipole-dipole interactions should occur up to about 60 mole per cent of acetic acid from where it starts de-association up to 30 mole per cent of acetic acid from where it must start slightly dissociating.

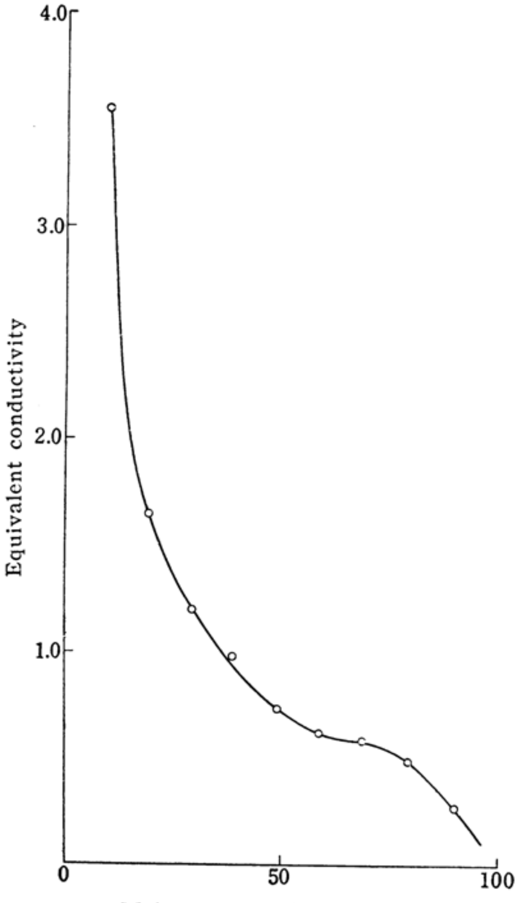

Fig. 3. Equivalent conductivity of ethylene-glycol-acetic acid system.

A plot of viscosity (column 5 of the Table) against percentage compositions (not shown) shows a gradual fall as mole per cent of acetic acid increases deviating from linearity with a convexity towards the axes.

Plots of refractive index and molar refractions (column 10 and 11) against mole per cent composition (not shown) show a gradual fall with increase in the mole per cent of acetic acid with a slight dip at 30 mole per cent of it.

A plot of volume contraction in c.c. against mole per cent composition (not given) shows an unsymmetrical parabola with a maximum at 30 mole per cent of acetic acid with a stationary value between 40 and 50 mole per cent of it.

Comparison of the behaviour of ethylene glycol-acetic acid system with those of aqueous boric acid and some polyhydric alcohols brings out a great dissimilarity. Perhaps the presence of water as an additional component and the basicity of the acid used may be among other contributing factors for the above dissimilarity.

Summary

Equivalent conductivity, volume contraction, viscosity, dielectric constant and

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[10] I. I. Zhukov and I. F. Karpova, *J. Gen. Chem.* (*U.S.S.R.*), 161-166, 6 (1936).

refractometric measurements of mixtures of ethylene glycol and acetic acid at different percentage compositions have been made. Probably a predominating dipole-dipole interaction occurs when ethylene glycol is added to anhydrous acetic acid up to about 60 mole per cent of the latter from where up to 30 mole per cent of acetic acid de-association seems to occur and from 30 mole per cent of acetic acid downwards slight dissociation is evidenced. This system is dissimilar in behaviour to those of aqueous boric acid and some polyhydric alcohols.

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