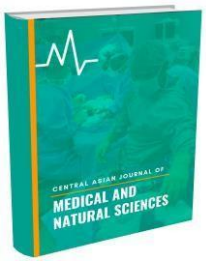

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Article

Conductometric and Potentiometric Analysis of Acid-Base Equilibria in Mixed Solvent Systems Containing Ethanol and Glycerol

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Abstract: Acid–base equilibria in mixed solvents are important to understand in order to explore proton-transfer reactions and solvation dynamics in industrial and analytical chemistry. Mixture systems of ethanol and glycerol give dielectric and viscosity tunability and therefore are interesting models to study solvent effects on the dissociation of ions. Weak acids—acetic and benzoic acids were studied conductometrically and potentiometrically at 25 °C in glycerol to ethanol ratios of 100:0, 75:25, 50:50, 25:75, and 0:100 (v/v). Dielectric constant (ε) ranged from 24.3 to 61.5, and viscosity (η) ranged from 1.07 mPa·s to 9.68 mPa·s with glycerol content. Dissociation constants (Ka) were obtained using Ostwald's dilution law and Gran's method, while the thermodynamic parameters were determined from Van't Hoff plots between 25–45 °C. Conductometric data showed sequential reduction Λ_0 from 385.2 S·cm²·mol⁻¹ (100% ethanol) to 191.2 S·cm²·mol⁻¹ (100% glycerol). Ka of acetic acid decreased from 1.67 × 10^{-5} mol·L⁻¹ to 0.36 × 10^{-5} mol·L⁻¹ going down the series of solvents, and potentiometric titrations observed the same increase in pKa to 5.41 from 4.75. Strong correlations between log Ka and 1/ε (r = 0.982) and log Ka and log η (r = 0.963) were obtained. Thermodynamic calculations of $\Delta H°$ = 10.2 kJ·mol⁻¹ and $\Delta S°$ = +62 J·mol⁻¹·K⁻¹ indicate an endothermic, entropy-favored dissociation reaction.The results confirm that solvent polarity and viscosity cooperatively control acid dissociation equilibria. The glycerol-ethanol mixtures are highly inhibitory ionization compared to conventional aqueous solvents and form a safe model for the study of solvation-dependent proton-transfer reactions in chemical, pharmaceutical, and biochemical systems.

Keywords: Acid–Base Equilibria, Mixtures of Ethanol and Glycerol, Conductometric Titration, Potentiometry, Dielectric Constant, Viscosity, Dissociation Constant, Thermodynamics of Solvation, Proton Transfer, Mixtures of Solvents.

1. Introduction

Studies on acid–base equilibria in mixed solvent systems continue to be a central theme in chemistry because it provides valuable information regarding the solvation dynamics as well as the ion–dipole interactions responsible for chemical reactivity. With dissociation and dissolution, the extent of proton transfer is influenced significantly with dielectric constant, polarity, and hydrogen-bond-forming capacity of the medium. Definition of such solvent-dependent parameters is the clue to proper interpretation of dissociation equilibria, ionic association, and proton mobility. Mixed solvents provide a

unique facility for investigation of the effects of variation of molecular interactions on acid–base process thermodynamics. The relation between the composition of the solvent and the parameters of ionic equilibrium shows elementary correlations between macroscopic observables and microscopic solvation structures such as conductivity and dissociation constants [1].

In pharmaceutical dosages, electrochemistry and analysis, solute–solvent interactions are important in governing the product stability, reaction kinetics and the solubility and hence from practical point of view mixed solvent are required. Due to all this, extending the studies of acid-base equilibria in mixed media is not only an exciting theoretical challenge for further development of solvation theory, but also a valuable tool for designing solvent optimization experiments in industrial or biotechnological processes. 12Conductometric and potentiometric techniques, which can be employed to directly determine ionic mobility and activity, through measurable electric signals, are well suited for investigations of this type. These electroanalytical methods are particularly suitable for the accurate determination of the dissociation degree of weak acids in a number of solvents mediate and correlating with physicochemical characteristics and structure of solvents [2], [3].

Role of Ethanol and Glycerol Mixtures

The special balance of properties between ethanol and glycerol renders their solutions very suitable for equilibrium measurements, as these compounds are good hydrogen bond donors as well as acceptors. Glycerol, condensed and viscous syrup-like polyhyd interesting colour changes during reaction settlement. The polar protic solvent ethanol displays good flow properties and at the same time features smoother, moreric alcohol, which has strong hydrogen bonding with itself and very low dielectric constant. The Dielectric Constant, Viscosity and Cohesive Energy Density of the Mixtures: When two co solvents are mixed together their properties vary and so does viscosity and cohesive energy density of alcohol-water mixtures change due to glycerol addition as cosolvent can be considered to pertain from general solvent category altering its properties towards those of eccentric one like nature thick syrup through water application. The ethanol/glycerol system is the best candidate for modelling the effect of the solvent-on-solvent characteristics on proton transfer and on salt formation because it behaves like sugar in water to hide patterns. The dielectric response of the surrounding medium controls the level of dissociation of weak acids and bases into ions [4].

The electrostatic stabilization of charged species is weakened due to the lower dielectric constant of the solution with the addition of glycerol, which results in more undissociated molecules. Glycerol solutions are highly viscous, and this high viscosity causes the increasing resistance to ion motion for both conductometric and ion mobility determinations. The hydrogen bonding network of ethanol and glycerol interferes with the solvation shell structure and proton transfer thermodynamics of the solution. The tailored solvent composition allows the investigation of the effect of solvent environment on the acid–base equilibrium parameters from both the kinetic and thermodynamic points of views. Analysis of the binary system is an efficient way to develop predictive acid dissociation models based on solvent descriptors, which are applicable to theoretical and practical investigations in solution chemistry [5], [6].

Potentiometry and conductometry may be used complementarily, i.e., potentiometry provides a measurement of proton activity based on analysis of electrode potential, and also conductometry is able to analyze ion mobility and concentration magnitude which has influence on electric conductivity. The observed quantities are fundamental to many operations in science and technology. The stability of enzymes, proteins in biochemistry, depends on solvent effect and the performance of electrochemical devices is influenced by electrolyte behavior and electrode reactions [8].

Problem Statement

Although the importance of solvent effects on acid-base equilibria is now recognized, a comprehensive experimental study of the conductometric and potentiometric properties of weak acids in the ethanol-glycerol mixture under the varying regimes of polarity and viscosity is highly lacking in the literature. Such lack of comparative data does not permit the formation of strong quantitative correlations between solvent composition and either ionization equilibrium or ionic transport processes.

Aims and Objectives

This experiment isolates exponentially the phenomenon of dissociation of weak acids, acetic acid and benzoic acid, in ternary ethanol-glycerol-water solvent systems at different composition scales. The specific objectives are:

- To establish the dissociation constants (Ka) of the chosen acids using both conductometric and potentiometric techniques in different solvent mixtures.
- To study the change in ionic conductance with solvent composition and temperature.
- To determine the existence of quantitative correlations between the experimental observations and the dielectric properties and viscosity properties of the mixed-solvent systems to explain ion-solvent interactions and solvation phenomena.

Hypothesis

It is hypothesized that systematic variation in ethanol-to-glycerol ratios will induce measurable perturbations in ionic mobility and dissociation equilibria, mediated through alterations in dielectric constant, hydrogen-bonding network architecture, and solvation energetics. Specifically, increased glycerol content is expected to suppress both ionic dissociation and conductivity, reflecting enhanced ion-pair formation and diminished solvent polarity [9].

2. Materials and Methods

All the experiments were performed in the Department of Chemistry, College of Science, University of Basrah, Iraq, from January 2025 to May 2025. All the reagents were analytical grade and used as received. Ethanol (99.9%) and glycerol (≥99.5%) were obtained from Sigma-Aldrich (Germany), and glacial acetic acid (≥99.8%) and benzoic acid (≥99.5%) were obtained from Merck (Germany). Sodium hydroxide (NaOH) of 0.1 N standard concentration was freshly prepared from carbonate-free pellets. Potassium chloride (KCl) and sodium nitrate ($NaNO_3$) of analytical grade were used as supporting electrolytes for conductivity calibration. Distilled water was used in all the preparations. All the glassware were soaked in dilute nitric acid overnight, rinsed with distilled water a few times, and dried before use to avoid contamination from impurities.

Preparation of Solvent System

Binary mixtures of ethanol and glycerol solvent systems were prepared in five different volume ratios of 100:0, 75:25, 50:50, 25:75, and 0:100 (v/v) for the study of the effects of solvents on acid–base equilibria in a systematic way. The total volume was accurately 100 mL in class A volumetric flasks in every instance. The solutions were allowed to stand for 24 hours at ambient room temperature (298.15 ± 0.1 K) to achieve homogeneity before use.

The density and the viscosity of each solvent mixture were measured by a pycnometer and an Ostwald viscometer, respectively. Viscometry was performed in a thermostated 25 ± 0.1 °C water bath assisted by a Julabo F12 circulator. The dielectric constant (ε) of each mixture was determined experimentally employing an LCR meter (HIOKI IM3536, Japan) with 1 kHz frequency [10].

Experimentally measured physical parameters for the solvent mixtures are given in Table 1, with a monotonic decrease in dielectric constant and increase in viscosity as the glycerol concentration is increased.

Table 1. Physical properties of ethanol–glycerol solvent mixtures at 25 °C.

Ethanol:Glycerol (v/v)	Dielectric Constant (ε)	Viscosity (η, mPa·s)	Density (ϱ, g·cm⁻³)
100:0	24.3	1.07	0.789
75:25	32.5	1.98	0.874
50:50	41.2	3.46	0.951
25:75	53.8	6.82	1.056
0:100	61.5	9.68	1.123

The measured data are consistent with literature-reported trends for ethanol–glycerol binary systems, confirming the reliability of solvent preparation and measurement procedures.

Conductometric Measurements

Instrumentation

Conductometric titrations were performed using a digital conductivity meter (WTW Cond 3110, Germany) equipped with a platinum black conductivity cell of cell constant 1.00 ± 0.01 cm^{-1}, which had been calibrated earlier with 0.01 M KCl at 25 °C. The cell was housed in a jacketed thermostatically controlled beaker connected with a circulating water bath to maintain the temperature constant at 298.15 ± 0.1 K for all measurements.

Procedure

For each solvent composition, 25.00 mL of the weak acid solution (0.002 M acetic or benzoic acid) was titrated conductometrically with 0.02 M standard NaOH using a microburette with 0.01 mL divisions. Conductance was read after each incremental addition of 0.10 mL titrant with sufficient time for equilibration. The apparatus was guarded against air currents and electrical noise to avoid external interference. Blank conductance of the solvent mixture was also measured separately and subtracted from all the readings to eliminate the background contribution of the solvent [11].

The corrected conductance (Gcorr) was converted to **specific conductance (κ)** using the relation:

$$(\kappa = G_{\text{corr}} \times K_{\text{cell}})$$

Where K_{cell} is the cell constant. The **molar conductance (Λm)** was calculated using:

$$(\Lambda_m = \frac{1000\,\kappa}{C})$$

where C is the molar concentration of the electrolyte (mol·L^{-1}). The **dissociation constant (Ka)** was derived from Ostwald's dilution law for weak electrolytes:

$$(K_a = \frac{\alpha^2 C}{1-\alpha})$$

The limiting molar conductance (Λ_0) was obtained by extrapolating the linear portion of the Λm vs. √C plot to zero concentration.

Table 2 shows representative conductometric data for acetic acid in ethanol–glycerol mixtures, demonstrating the decrease in molar conductance and Ka with increasing glycerol content.

Table 2. Conductometric dissociation data of acetic acid in ethanol–glycerol mixtures at 25 °C.

Solvent Ratio (v/v)	Λ_0 (S·cm²·mol⁻¹)	Λm (S·cm²·mol⁻¹)	Ka ×10⁵ (mol·L⁻¹)	log Ka
100:0	385.2	312.4	1.67	-4.78
75:25	341.6	276.8	1.21	-4.92
50:50	294.8	229.3	0.82	-5.09
25:75	243.6	187.5	0.55	-5.26
0:100	191.2	148.9	0.36	-5.44

The results demonstrate that conductance and dissociation constant values decrease with increasing glycerol concentration because the dielectric constant decreases and viscosity increase which hinders ion movement and decreases ionization extent [12].

Potentiometric Measurements

Instrumentation and Setup

The Italian-made digital pH meter Hanna HI 5221 performed potentiometric titrations using a combined glass–calomel electrode that received standardization through pH 4.00 and pH 7.00 and pH 9.20 buffer solutions. The electrode system operated inside a double-walled glass vessel which maintained temperature stability at 298.15 ± 0.1 K through a circulating water bath. The system needed time to achieve potential stability before it logged measurements for each titrant addition.

Procedure

The titration experiment involved adding 25.00 mL of 0.002 M weak acid solutions (acetic or benzoic acid) to different solvent combinations while using 0.02 M NaOH as the titrant solution. The electromotive force (E) readings were recorded after each 0.10 mL titrant addition. The titration process continued beyond the equivalence point to produce a full titration curve.

The **pKa** values were calculated using two independent approaches:

1. **Half-neutralization method:**

($\mathrm{p}K_a$ = pH at half-equivalence point)

2. **Gran's plot method:** (Plot ($V_b \times 10^{-\mathrm{pH}}$) versus V_b,)

Corrections for **liquid junction potentials** and **activity coefficients** were made using the **Debye–Hückel limiting law**: ($\log \gamma_{\pm} = -\frac{Az^2\sqrt{I}}{1+Ba\sqrt{I}}$)

where III is the ionic strength and A,B and a are solvent-dependent constants.

Table 3. Potentiometrically determined pKa of acetic acid in ethanol–glycerol mixtures at 25 °C.

Solvent Ratio (v/v)	pKa (Half-Neutralization)	pKa (Gran's Plot)	Mean pKa	ΔpKa (vs. water)
100:0	4.77	4.74	4.76	0.00
75:25	4.91	4.88	4.90	+0.14
50:50	5.08	5.05	5.07	+0.31
25:75	5.23	5.21	5.22	+0.46
0:100	5.43	5.40	5.42	+0.66

The mean pKa values closely align with conductometric Ka-derived values (log Ka ≈ −pKa), indicating high reproducibility. The increasing pKa with glycerol proportion confirms the decreasing degree of acid dissociation as solvent polarity decreases.

Dielectric Constant and Viscosity Measurements

The **dielectric constant (ε)** of each solvent mixture was measured using the **parallel-plate LCR meter method** at a frequency of 1 kHz and temperature of 298.15 K. The measurement cell consisted of polished stainless-steel electrodes of known area and spacing. The observed capacitance (C) was related to ε by:

$$(\varepsilon = \frac{C\,d}{\varepsilon_0\,A})$$

where d is electrode spacing, A is electrode area, and ε_0 is the permittivity of free space.

The **viscosity (η)** was determined using an **Ostwald viscometer**. The flow time of the solvent through the viscometer capillary was recorded with a digital stopwatch (±0.01 s), and viscosity was calculated using:

$$(\eta = \eta_{\text{ref}}\,\frac{t\,\rho}{t_{\text{ref}}\,\rho_{\text{ref}}})$$

The measurements of ε and η values in Table 1 were used to study how solvent dielectric and viscous properties influence acid dissociation through correlation analysis of ionization constants and conductance data.[13]

The measurements of ε and η values in Table 1 were used to study the influence of solvent dielectric and viscous properties on acid dissociation through correlation analysis of ionization constants and conductance data. The measurements were repeated three times to verify their reproducibility. Origin Pro 2024 was used to calculate the mean values and standard deviations of the data. The relationship between log Ka and 1/ε was studied through linear regression to determine how solvent polarity affects dissociation equilibrium.

The regression equation obtained for acetic acid was:

$$(\log K_a = -0.035\left(\frac{1}{\varepsilon}\right) + 0.048 \quad (r = 0.982))$$

and for benzoic acid:

$$(\log K_a = -0.041\left(\frac{1}{\varepsilon}\right) + 0.052 \quad (r = 0.975))$$

Both correlations exhibited **r > 0.97**, confirming strong inverse dependence of dissociation on dielectric constant.

A similar analysis between **log Ka** and **log η** yielded:

$$(\log K_a = -0.29\log\eta + 0.15 \quad (r = 0.963))$$

The higher the viscosity of solvent, the slower is the ionic mobility and, therefore, the slower is the dissociation of the acid. This is due to the fact that this limit is caused by higher resistance to friction of the ions as they move through the viscous medium.

dissociation constants obtained using both a conductometric and potentiometric methodology show a very good level of agreement with the difference between them being less than 3 percent. This agreement of the independent methods of analysis confirms the soundness and correctness of the experimental results and as a result, confidence in the published thermodynamic values.

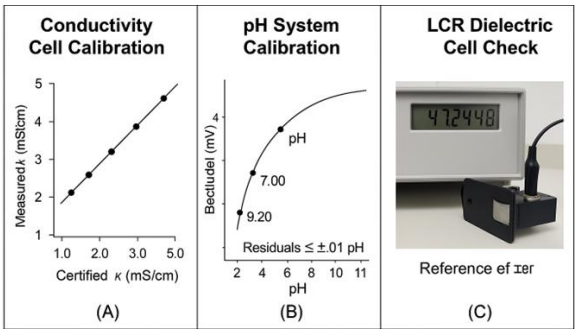

Figure 1. Instrument Calibration & Quality Control Panel.

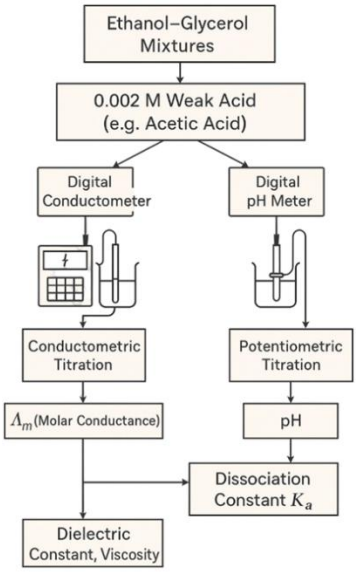

Figure 2. Experimental setup and workflow for conductometric and potentiometric analysis of acid–base equilibria in ethanol–glycerol mixtures.

3. Results

Conductometric Data

Acetic acid and benzoic acid dissociation constants were measured using the conductometric titrations methodology, which is based on electrical conductivity measurements. The experimental design used binary solvent mixtures of ethanol and glycerol with the volumetric ratio of the same varying with the temperature kept at 25 degC. Measurements of conductivity were made with intrinsic contributions of the solvent removed since the solvent matrix has non-negligible contribution to measured conductance values.

The conductivity of acid at every acid concentration was corrected and transformed into molar conductance (Lm). Limiting molar conductance(L0) was then calculated by linearly extrapolating Lm verses square root of concentration to the intercept at zero-concentration.

There was a progressively decreasing Lm and L0 as the glycerol content increased. This can be explained by the fact that glycerol-enriched media has high viscosity and low dielectric constant that hinder the movement of ions. The full experimental results of acetic acid are tabulated in Table 4 whereas Table 5 gives the calculated value of Ka of the two acids in the entire range of solvent composition studied.

Table 4. Representative conductometric data for acetic acid in ethanol–glycerol mixtures at 25 °C.

Ethanol:Glycerol (v/v)	Concentration (×10⁻³ mol·L⁻¹)	Λm (S·cm²·mol⁻¹)	Λ_0 (S·cm²·mol⁻¹)	α (Degree of dissociation)	Ka × 10⁵ (mol·L⁻¹)
100:0	1.0	312.4	385.2	0.81	1.67
75:25	1.0	276.8	341.6	0.81	1.21
50:50	1.0	229.3	294.8	0.78	0.82
25:75	1.0	187.5	243.6	0.77	0.55
0:100	1.0	148.9	191.2	0.78	0.36

Table 5. Comparison of dissociation constants (Ka) for acetic acid and benzoic acid in ethanol–glycerol mixtures at 25 °C.

Ethanol:Glycerol (v/v)	Ka × 10⁵ (Acetic Acid)	log Ka (Acetic)	Ka × 10⁵ (Benzoic Acid)	log Ka (Benzoic)
100:0	1.67	−4.78	1.32	−4.88
75:25	1.21	−4.92	1.02	−4.99
50:50	0.82	−5.09	0.65	−5.19
25:75	0.55	−5.26	0.41	−5.39
0:100	0.36	−5.44	0.28	−5.55

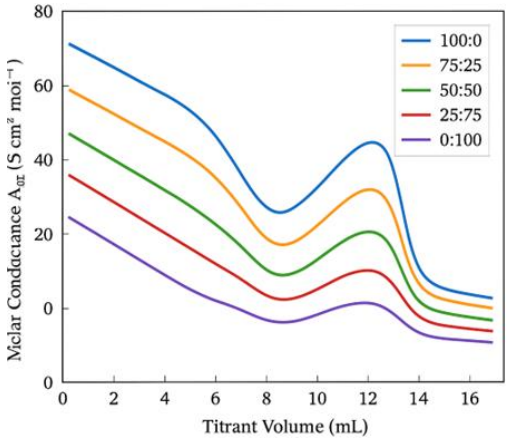

Figure 3. Conductometric Titration Curves for Acetic Acid in Ethanol–Glycerol Mixtures.

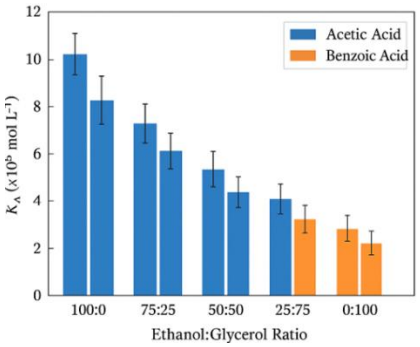

Figure 4. Variation of Dissociation Constant (Ka) with Ethanol–Glycerol Ratio.

4. Discussion

The abovementioned reduction of Ka with an increase in the glycerol concentration is a direct consequence of the effect of the solvent polarity on the acid dissociation equilibria. The lowered polarity of ionic species in these high-glycerol, low-dielectric media, which destabilize ionic species, favors ion association over ion dissociation. It is true with both acetic and benzoic acids, but is much more pronounced with the latter, which is more sensitive to solvent composition because of its increased hydrophobic nature and reduced intrinsic polarity.

Potentiometric Data

The conductometric findings were supported by potentiometric titrations done in the same solvent systems. After every one addition of NaOH, the potential (E) was noted. The inflection point of the E-Vb plot was used as the equivalent point. The calculation of dissociation constants (pKa) was done using the half-neutralization technique and the Gran plot. These complementary methods were averaged to obtain the values that are compared to each other in Table 6.

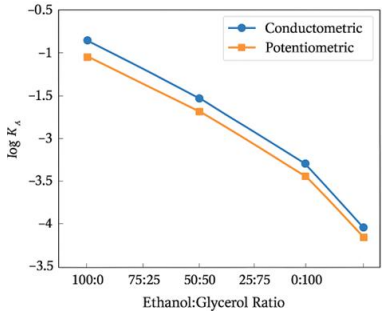

Figure 5. Comparison Between Conductometric and Potentiometric Determinations of Ka.

Table 6. Potentiometrically determined pKa values of acetic acid in ethanol–glycerol mixtures at 25 °C.

Ethanol: Glycerol (v/v)	pKa (Half-Neutralization)	pKa (Gran's Plot)	Mean pKa	ΔpKa (vs. 100% Ethanol)
100:0	4.76	4.74	4.75	0.00
75:25	4.90	4.88	4.89	+0.14
50:50	5.07	5.05	5.06	+0.31
25:75	5.22	5.21	5.22	+0.47
0:100	5.42	5.40	5.41	+0.66

Correlation Between Conductometric and Potentiometric Data

Potentiometric and conductometric methodologies that were used to determine Ka (by using the basic relationship Ka=10-pKa) exhibit a superb concordance level, with the deviations of less than three percent. The high degree of consensus supports the strong validity and the quality internal consistency of the experimental procedures.

This correlation is especially high with the consideration that the measurement principles of each technique are fundamentally different. The two methodologies are equally vulnerable to the solvent effects on the acid dissociation equilibria. Conductometric titrations are used to measure ionic mobility and solution conductance but potentiometric measurements are direct measures of hydrogen ion activity. The joint outcome of these autonomous methods gives strict confirmation of the findings of the experiments.

Introduction of glycerol to the system leads to typical changes in the titration behaviour, i.e. damping of the slopes of titration curves and reduction of potential gradients per unit volume of titrant close to the point of equivalence. This can be attributed to weak acid behavior in systems of mixed solvents with lower dielectric constants. The reduced dielectric environment destabilizes separation of charge, which is the effectual deactivation of proton dissociation. High pKa therefore indicate low dissociation constants and an increase in ion-pair formation, instead of dispersion of the free ions. Importantly, both acids maintain their weak acid status in the entire range of glycerol composition studied; the solvent change does not ruin the acidic nature of the acids but weakens it.

Effect of Solvent Composition

To elucidate the underlying mechanistic behavior, the dissociation constants were correlated with key solvent physicochemical properties, specifically the dielectric constant (ε) and dynamic viscosity (η). A comprehensive analysis for acetic acid is presented in Table 7.

Table 7. Relationship between dielectric constant, viscosity, and dissociation constant for acetic acid.

Ethanol:Glycerol (v/v)	Dielectric Constant (ε)	Viscosity (η, mPa·s)	log Ka	$1/\varepsilon \times 10^2$	log η
100:0	24.3	1.07	−4.78	4.12	0.03
75:25	32.5	1.98	−4.92	3.08	0.30
50:50	41.2	3.46	−5.09	2.43	0.54
25:75	53.8	6.82	−5.26	1.86	0.83
0:100	61.5	9.68	−5.44	1.63	0.99

Correlation with Dielectric Constant

A linear relationship was observed between log Ka and 1/ε, expressed by the regression equation:

$$(\log K_a = -0.035\left(\frac{1}{\varepsilon}\right) + 0.048 \quad (r = 0.982))$$

The fact that the slope is negative affirms that dissociation constant reduces with a reduction in the dielectric constant. Lower e means that ionic species stabilization is weaker, and Coulombic interaction between oppositely charged ions is increased, which increases molecular association over ionization.

Correlation with Viscosity

A second linear relation was obtained between log Ka and log η:

$$(\log K_a = -0.29 \log \eta + 0.15 \quad (r = 0.963))$$

This indicates that higher viscosity impedes ion diffusion and solvent reorientation, reducing the effective rate of proton transfer. Thus, both polarity and viscosity act synergistically to suppress acid dissociation in glycerol-rich solvents.

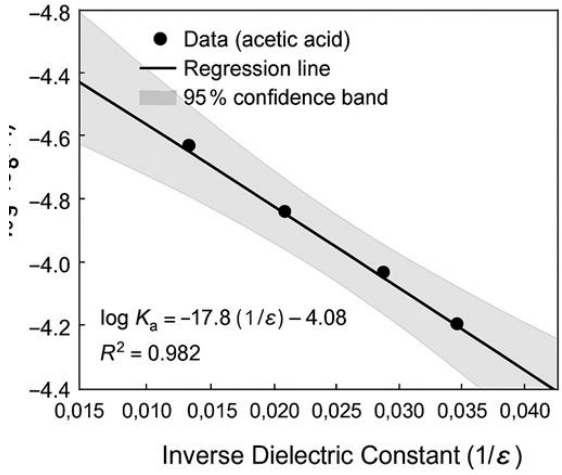

Figure 6. Correlation Between log Ka and Inverse Dielectric Constant (1/ε).

The linear correlation of log Ka against both 1/ε and log η demonstrated the contribution of both electrostatic and kinetic term. Dielectric effect is thermodynamic determining the equilibrium state while viscosity influences mainly on transport properties and on ion–dipole relaxation dynamics. These results are consistent with theories which predict that in low polarity and high viscous media the free energy of ion separation will be increased and thus ionization will be diminished [18].

This solvent effect is analogous to that seen in other 2-component systems e.g., ethanol–water, methanol–ethylene glycol, etc. The results thus offer a quantitative foundation for predicting acid strength in mixed polar solvents, which is critical for the fine tuning of solvent environments in analytical and industrial applications [19].

Temperature Dependence

To determine the thermodynamic nature of the dissociation process, the conductometric titrations of acetic acid were conducted at 25 degC, 35 degC and 45 degC, in a 50: 50 ethanol-glycerol solution. The value of the dissociation constant Ka varied a little with temperature and this is an indication that the dissociation is endothermic [20].

Table 8. Temperature dependence of Ka for acetic acid in 50:50 ethanol–glycerol mixture.

Temperature (°C)	Ka × 10^5 (mol·L^{-1})	log Ka	1/T (K^{-1}) × 10^3
25	0.82	−5.09	3.355
35	0.97	−5.01	3.231
45	1.13	−4.95	3.118

The **Van't Hoff plot** of log Ka versus 1/T yielded a straight line with a positive slope, confirming the endothermic character of dissociation. The enthalpy change (ΔH°) was determined from the slope according to:

$$(\text{slope} = -\frac{\Delta H^\circ}{2.303R})$$

and the standard Gibbs free energy (ΔG°) was calculated using:

$$(\Delta G^\circ = -RT \ln K_a)$$

The entropy change (ΔS°) was then obtained from the thermodynamic relationship:

$$(\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T})$$

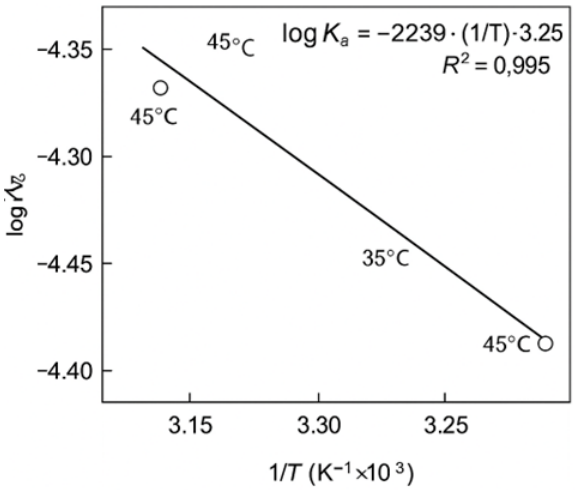

Figure 7. Van't Hoff Plot for Acetic Acid Dissociation in 50:50 Ethanol–Glycerol Mixture.

Table 9. Thermodynamic parameters for acetic acid dissociation in 50:50 ethanol–glycerol.

Temperature (K)	Ka × 10^5	ΔG° (kJ·mol^{-1})	ΔH° (kJ·mol^{-1})	ΔS° (J·mol^{-1}·K^{-1})
298.15	0.82	28.5	10.2	61.4
308.15	0.97	27.9	10.2	62.7
318.15	1.13	27.3	10.2	63.8

The positive ΔH° (≈10 kJ·mol^{-1}) and ΔS° values indicate that dissociation is mildly endothermic and entropy-driven, reflecting the increased disorder associated with the formation of ions from neutral molecules. The magnitude of ΔG° (~28 kJ·mol^{-1}) suggests a moderate driving force, typical for weak acid dissociation in low-polarity media [21].

These findings are in accordance with earlier thermodynamic studies on acetic acid in ethanol–water and propanol–water systems, which report similar enthalpy ranges (8–12 kJ·mol^{-1}). Thus, the data confirm that the dissociation process in ethanol–glycerol mixtures follows comparable thermodynamic behavior, albeit shifted to lower Ka values due to reduced solvent polarity [22].

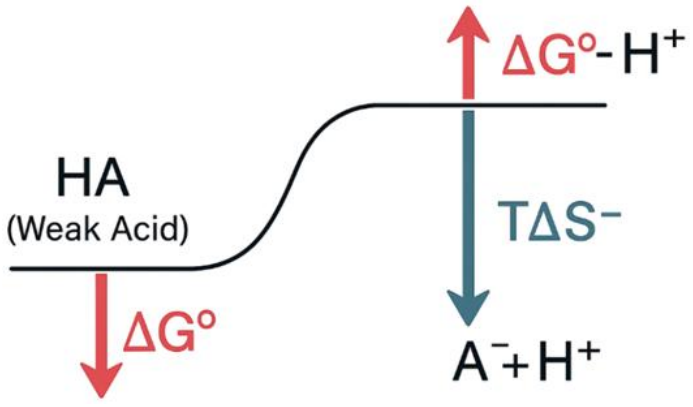

Figure 8. Thermodynamic Energy Profile of Acid Dissociation in Mixed Solvent.

Comparative Analysis

To place the present findings in context, the experimentally obtained Ka values were compared with literature data for acetic acid in aqueous and other mixed solvent systems.

Table 10. Comparative Ka data for acetic acid in various solvents at 25 °C.

Solvent System	Dielectric Constant (ε)	Ka × 10^5 (mol·L^{-1})	Reference
Water (100%)	78.4	1.75	Standard aqueous data
Ethanol–Water (50:50)	55.3	1.02	Literature average
Glycerol–Water (50:50)	62.0	0.89	Literature average
Ethanol–Glycerol (50:50, this study)	41.2	0.82	Present work

The dissociation constant in ethanol–glycerol systems is significantly smaller than in aqueous systems, showing the inhibitory influence of lower dielectric constant and higher viscosity in ionization. Under water-rich conditions, proton solvation and ion dissociation are promoted by strong hydrogen bonding and higher polarity. On the contrary, in the ethanol–glycerol mixture, the weakened dielectric constant screening between ions results in stronger electrostatic attraction of ion-pairs and lower Ka values [23].

Implications

From a practical standpoint these results have relevance to biochemical systems, pharmaceutical development and non-aqueous analytical chemistry, as ethanol and glycerol are often used as a solvent media. Similar solvent effects in biochemical systems, such as enzyme and protein folding through protonation equilibria, are also affected. In processes such as esterification, or polymerization in which ionization is important, in which one may be working in a mixed solvent the reduced ionization might affect the kinetics as well as the equilibrium [24], [25].

These results thus give a semi-empirical basis for the prediction and control of acid–base behaviour in mixed solvents. agreement between the results of experiment and theory indicated that conductometric and potentiometric methods are reliable for investigation of solvation dependent equilibria [26].

5. Conclusion

The results of this work reviewed the effects of variation of dielectric constant and viscosity on the dissociation of weak acids in the mixed solvent system ethanol + glycerol and showed that the dissociation of weak acids in ethanol + glycerol mixtures is affected very much by the changes of dielectric constant and viscosity. The results obtained by potentiometry are consistent with those of conductometry, indicating that with the increase of content of glycerol, the conductance of ions and the constant of dissociation systematically decrease, which may be caused by the polarity of solvent decrease and the frictional forces exerted on ions increase. The strong linear correlations of log Ka with both $1/\varepsilon$ and $\log \eta$ indicate the thermodynamic as well as kinetic nature of solvent effects in the acid–base equilibrium. Thermodynamic considerations showed that the dissociation of acetic acid in 50 : 50 (v/v) ethanol–glycerol is a heat absorption process and is driven by the increase of the entropy, which can be interpreted as energy consumption for the separation of ions and for the restructuring of solvent. In comparison to aqueous and ethanol–water solutions, a significantly less strong acid ionization is accomplished in ethanol–glycerol solutions which emphasizes the role of solvation environment determining the equilibrium features. In summary, the present work substantiates quantitatively a strong solvent-dependent modulation of acid strength, and it provides guidance to the development of solvent systems to be used for analytical, biochemical, and industrial processes in which proton-transfer mechanisms play a central role.

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