

Measurement of Excess Thermodynamic Functions from Viscosity Data

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Summary: Relative viscosities for formic, acetic, propionic and butyric acids in aqueous solutions were determined using thermostatic Ubbelohde flow viscometer in temperature range of 25 to 65°C. Excess viscosity, excess volume and activation parameter were calculated. It seems that as excess volume decreases with the rise of mole fraction of the particular acid and the corresponding excess viscosity increases. The effect of temperature on excess viscosity is much more telling than the same effect on ΔV^E . The explanation of this behaviour appears to be in the fact that with rise of temperature the intermolecular forces between acid-acid, acid-solvent and solvent-solvent change significantly to effect the viscosity behaviour, whereas for excess interactions as a function of temperature seems to get in different directions. This behaviour is well known for a liquid containing hydrogen bonds.

Introduction

The behaviour of associated liquids [1-2] as hydroxylic compounds is abnormal in several aspects; the viscosities are very much higher than for analogous non associated substances and the values decrease rapidly with increasing temperature. For example H₂O is more viscous than H₂S or CH₄, C₂H₅OH and C₂H₅NH₂ are much more viscous than propane, aniline and phenol are much more viscous than toluene. This abnormally large viscosity is of course due to hydrogen bonded structure of these carboxylic acids. When molecules in such liquids flows it must not only break vander waals and dipole bonds but also hydrogen bonds. The energy of activation for viscous flow is not only independent of temperature [3] as temperature is raised there is decrease in number of hydrogen bonds, to be broken before flow can occur, and hence the activation energy decreased when the compound contain two or more hydroxyl groups. The viscosity of the compounds is very much high on accounts of relatively large number of hydrogen bonds which must be broken in the formation of activated molecules for flow.

The present paper deals with investigations of thermodynamic and transport properties of binary liquid mixtures. The trends of changes have been

interpreted in terms of difference in size of the molecules and the strength of interaction taking place between the components of the mixtures. The excess viscosity η^E , excess volume ΔV^E were calculated. Free energy of activation δG^\ddagger , activation entropy δS^\ddagger and activation enthalpies δH^\ddagger were also evaluated from the experimental results on densities and viscosities for the aqueous system of formic, acetic, propionic and butyric acid at different temperature from 25°C to 65°C. Explanation of these quantities in terms of acid-acid, acid-water and water-water interactions have been given with special emphasis on hydrogen bonding in solutions [4-5].

Experimental

All densities of pure and mixture liquids were determined by pycnometer at various temperatures. The precision capillary of the pycnometer tube was calibrated against pure benzene and acetone. The temperature variation occurred in the range of $25.00 \pm 0.005^\circ\text{C}$.

A Townson Mercer thermostat, which was provided with an electrically driven stirrer, a heating coil, a constant thermoregulator, and a Be-

ckman thermometer, was used for temperature controlled measurements. The temperature of the bath was kept constant by means of heating coil, and a constant circulation of water was maintained for a particular reading. Details of experimental procedure is published elsewhere [6].

The viscosity measurements were made by using Ubbelohde viscometer [7] having a fine capillary with flared ends in order to minimize kinetic energy corrections. The times of flow were measured at least three times for each solution and agreed to within ± 0.2 s.

All acids were from E. Merck and were used as such.

Calculation and Results

Excess viscosity η^E and excess volume δV^E were calculated for the binary systems of formic, acetic, propionic and butyric acids with water at various temperatures from 25 to 65°C through the following equation.

$$V = (X_1M_1 + X_2M_2)/\rho \dots\dots (1)$$

$$V^E = [X_1M_1 + X_2M_2/P] - [X_1M_1/P_1 + X_2M_2/P_2] \dots\dots\dots (2)$$

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \dots\dots (3)$$

Where ρ , η and V are the density, viscosity and molar volume of the mixture, M_1 , M_2 , ρ_1 , ρ_2 , η_1 , η_2 are the molecular masses densities and viscosities of pure component 1 and 2 respectively.

Various thermodynamic parameters of viscous flow were determined using the Eyring [8] equation in the form as:

$$\ln \eta = [\ln A - \delta S^*/R] + \delta H^*/RT \dots\dots (4)$$

Where the symbols have their usual meaning. Value of $A = 10^{-3}$

When $\ln \eta$ is plotted against $1/T$ a straight line is obtained having slope equal to $\delta H^*/R$ and the intercept is equal to $-\delta S^*/R$. The standard free energy of activation δG^* for viscous flow is obtained using the equation:

$$\delta G^* = \delta H^* - T\delta S^* \dots\dots (5)$$

Discussion

The system of carboxylic acid and water can be classified as a polar and associated [9-10]. In non electrolyte systems positive deviation from ideal behaviour are attributed to dispersion forces [11] and negative deviations to the geometric considerations [12]. An attempt have made to explain the behaviour of liquid mixtures on the basis of sign and magnitude of excess viscosity η^E and excess volume δV^E which have been calculated by using equation 1 and 2. Here excess quantity (δV^E , η^E) are plotted against mole fraction of acid concentration.

Examination of figures (1-7) shows that the values η^E are positive. As the carboxylic acid concentration is increased the values of η^E reaches a

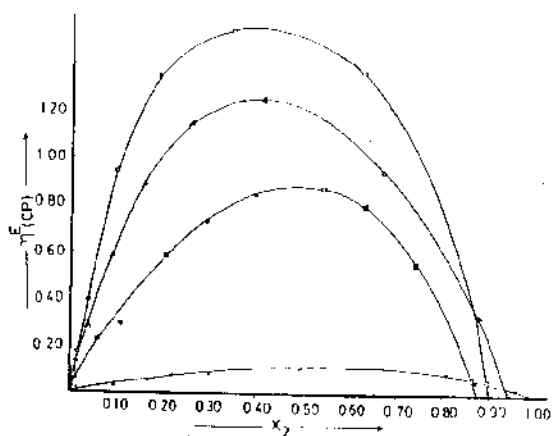


Fig.1: Plot of excess viscosity (η^E) vs mole fraction (X_2) of (x) formic acid + water, (⊕) acetic acid + water, (Δ) propionic acid + water and (O) butyric acid + water at 32°C.

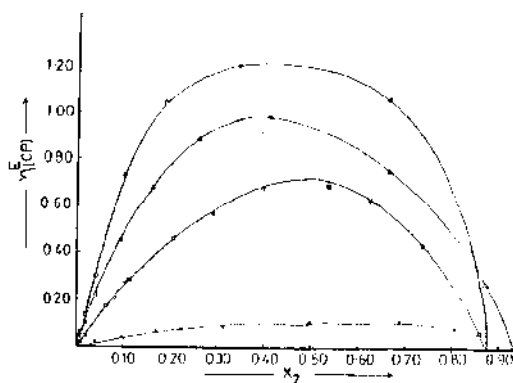


Fig.2: Plot of excess viscosity (η^E) vs mole fraction (X_2) of (x) formic acid + water, (⊕) acetic acid + water, (Δ) propionic acid + water and (O) butyric acid + water at 40°C.

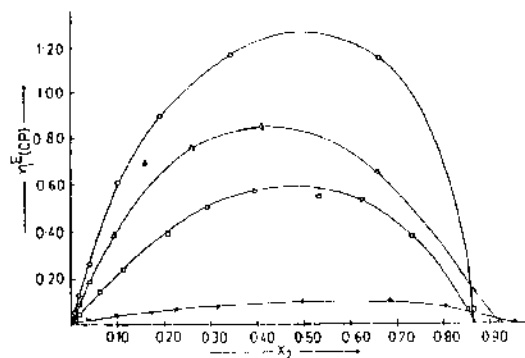


Fig. 3: Plot of excess viscosity (Δ^E) vs mole fraction (X_2) of (x) formic acid + water acetic acid + water () (Δ) propionic acid + water and (O) butyric acid + water at 45°C.

maximum at 1.44, 0.873, 1.44 and 1.546 cP at 32°C. The maximum appear at 0.4 mole fraction of propionic acid and 0.5 mole fraction of formic, acetic and butyric acid respectively. By increasing the temperature from 25 to 65°C at interval of 5°C the values of η^E decreases. The maximum values 0.144, 1.10, 1.56 and 1.930 cP of these carboxylic acids at 25°C decreased to 0.1030, 0.336, 0.481 and 0.577 cP at 65°C. According to Fort and Moore [13] the values of η^E are negative for a system of different molecular size in which dispersion forces are dominant.

In our system the η^E values are increase by addition of acid and this shows the magnitude of interaction increase with increase in concentration. In

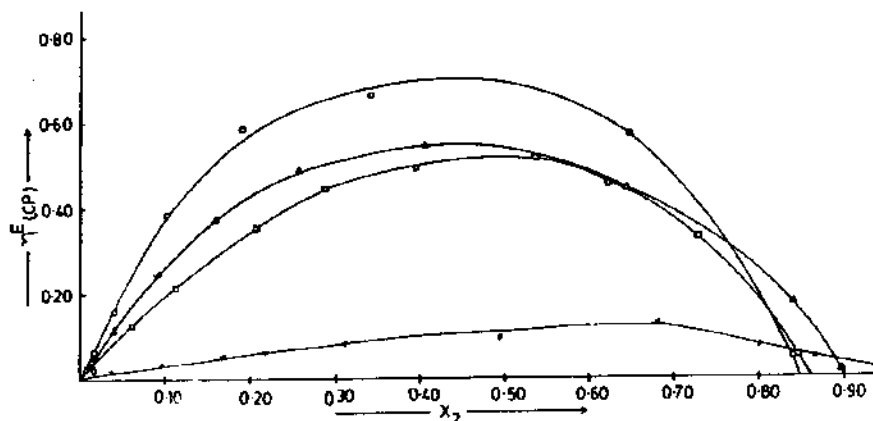


Fig. 4: Plot of excess viscosity h^E vs mole fraction (X_2) of (x) formic acid + water (p) acetic acid + water. (Δ) propionic acid + water and (O) butyric acid + water at 50°C.

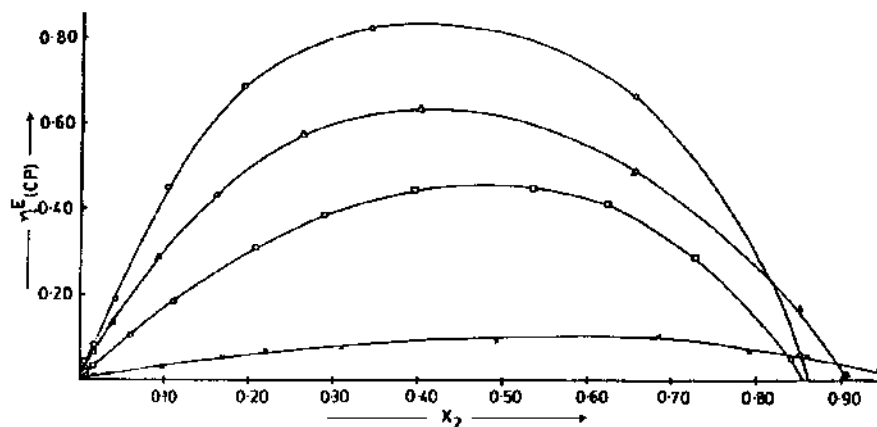


Fig. 5: Plot of excess viscosity (η^E) vs. mole fraction (X_2) of (x) formic acid + water (o) acetic acid + water (Δ) propionic acid + water and (O) butyric acid + water at 55°C.

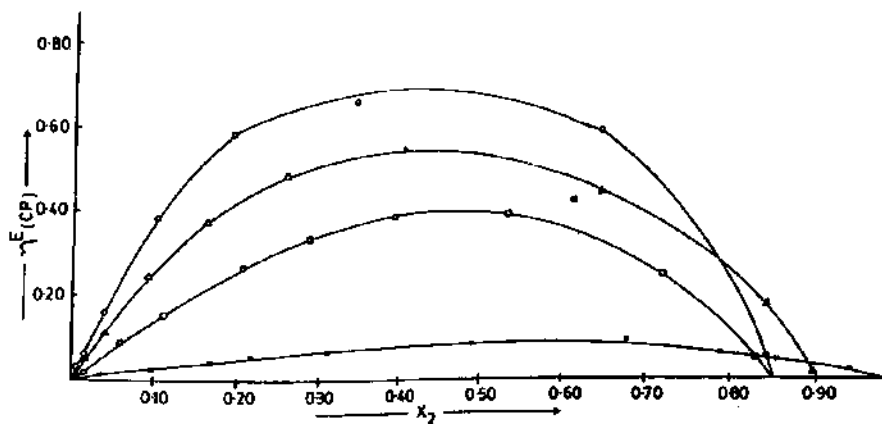


Fig.6: Plot of excess viscosity (η^E) vs mole fraction (X_2) of (x) formic acid + water (●) acetic acid + water (Δ) propionic acid + water and (○) butyric acid + water at 60°C.

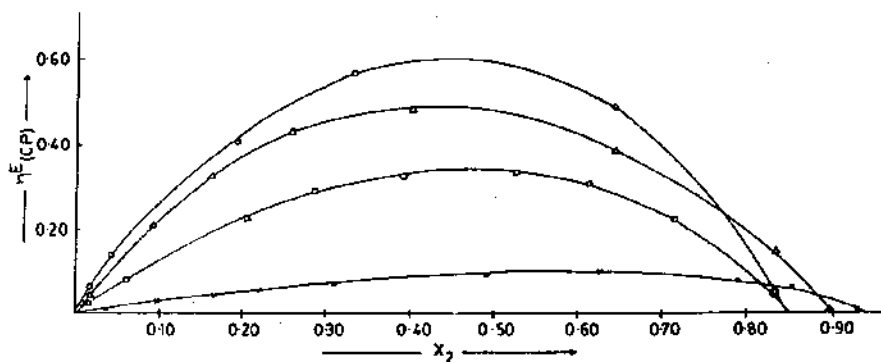


Fig.7: Plot of excess viscosity (η^E) vs. mole fraction (X_2) of (x) formic acid + water (●) acetic acid + water (Δ) propionic acid + water and (○) butyric acid + water at 65°C.

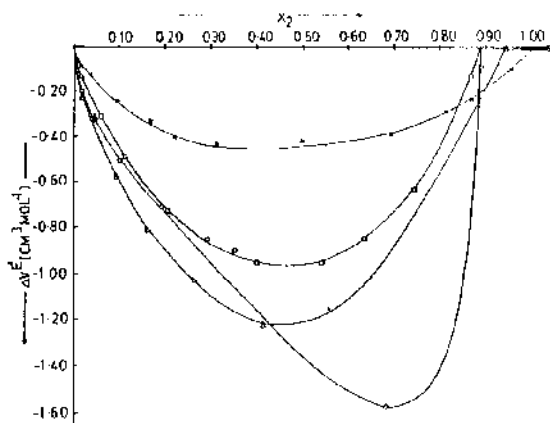


Fig.8: Plot of excess volume (ΔV^E) vs. mole fraction (X_2) of x formic acid + water acetic acid + water propionic acid + water and butyric acid + water at 25°C

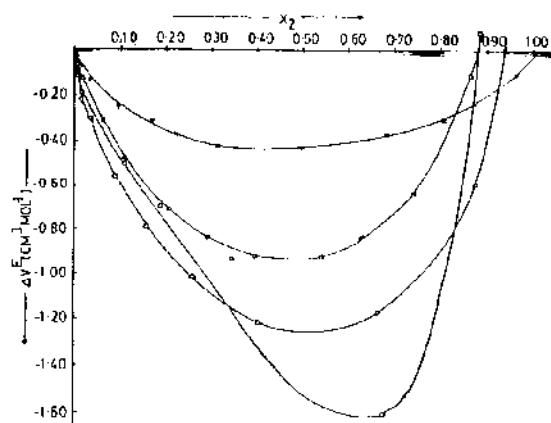


Fig.9: Plot of excess volume (ΔV^E) vs mole fraction (X_2) of (x) formic acid + water (●) acetic acid + water (Δ) propionic acid + water and (○) butyric acid + water at 32°C.

the present case all the chemical species being aliphatic, a small difference in size changes the excess viscosity to a large extent. The η^E is more positive for butyric acid than for other acids. For mixture of carboxylic acids with water for various mole fraction, η^E has the sequence.

Butyric acid > Propionic acid > Acetic acid > Formic acid

This trend in values of η^E give evidence in favour of increasing extent of specific interaction of these acids with water having an increased number of $-CH_2-$ substituents attached to $-C-OH$ group.

In figures (8-14) we compare the magnitude of δV^E in four binary mixture of carboxylic acids and water. Several effects may contribute [14] to the values of δV^E . In the system studied here, we can recognise four different effects as being important.

- 1) the breaking of liquid order on mixture.
- 2) unfavourable interactions between groups.
- 3) differences in molecular volume.
- 4) differences in free volume between liquid components.

The effect which is expected to act on δV^E , is difference in molecular sizes leads to interstitial accommodation in the mixture and hence to negative contribution to δV^E . The molecules of $HCOOH$ are the smallest of all other acids. Butyric acid has

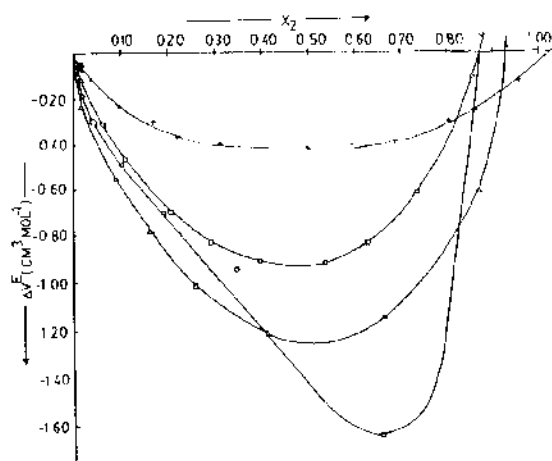


Fig.10: Plot of excess volume (ΔV^E) vs. mole fraction (X_2) of (x) formic acid + water, (□) acetic acid + water (Δ) propionic acid + water and (O) butyric acid + water at 40°C.

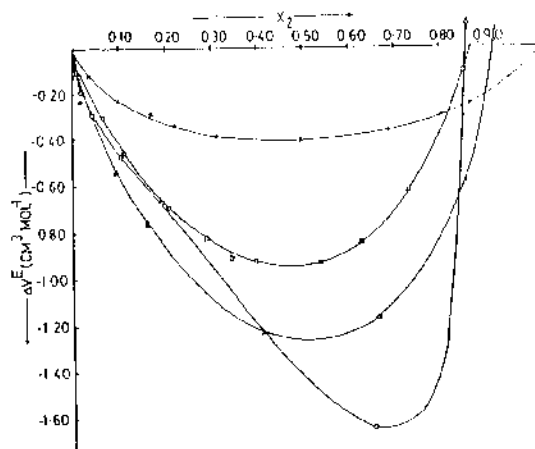


Fig.11: Plot of excess volume (ΔV^E) vs mole fraction (X_2) of (x) formic acid + water, (□) acetic acid + water (Δ) propionic acid + water and (O) butyric acid + water at 45°C.

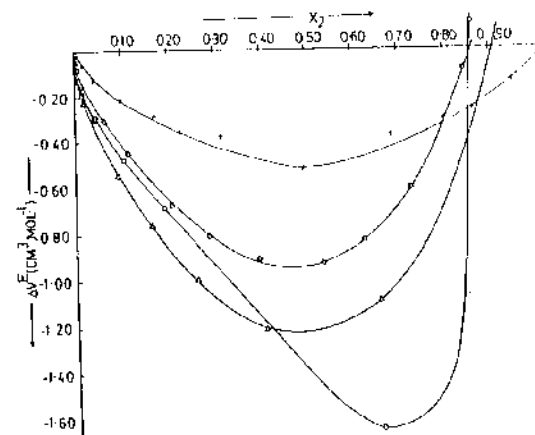


Fig.12: Plot of excess volume (ΔV^E) vs mole fraction (X_2) of (x) formic acid + water, (□) acetic acid + water (Δ) propionic acid + water and (O) butyric acid + water at 50°C.

the largest molar volume $84.68 \text{ cm}^3 \text{ mol}^{-1}$ than other acids whose molar volumes are 37.118 , 51.875 and $71.903 \text{ cm}^3 \text{ mol}^{-1}$ of formic, acetic and propionic acid respectively. The negative contribution to δH^E due to interstitial accommodation should be larger in the case of butyric acid. By increasing temperature the volume contraction (negative value of excess volume) decreases.

Another effect also of structural nature, and which again should give a negative contribution to δV^E is the difference in free volume components.

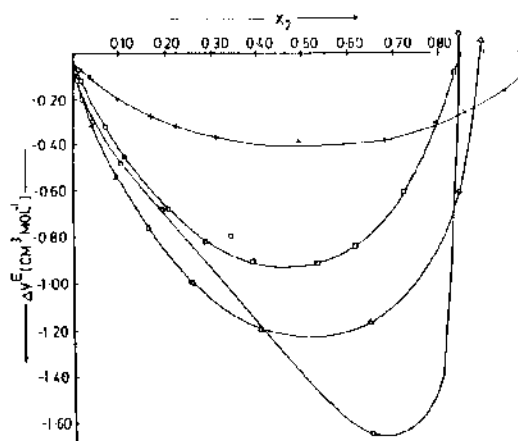


Fig.13: Plot of excess volume (ΔV^E) vs mole fraction (X_2) of (x) formic acid + water (□) acetic acid + water (Δ) propionic acid + water and (o) butyric acid + water at 60°C.

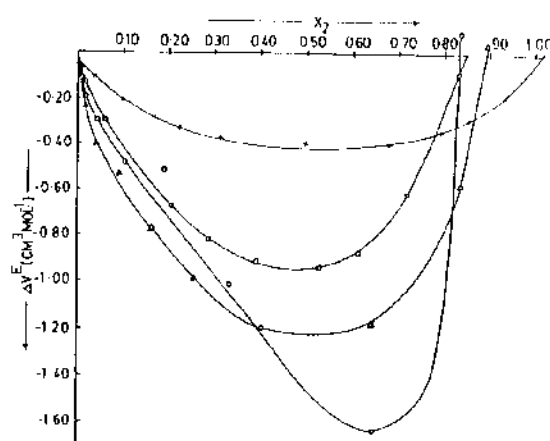


Fig.14: Plot of excess volume (ΔV^E) vs mole fraction (X_2) of (x) formic acid + water, (□) acetic acid + water (Δ) propionic acid + water and (o) butyric acid + water at 65°C.

Table-1: Activation parameter for viscous flow

| System | Concentration (M) | ΔH^\ddagger | $-\Delta S^\ddagger$ | ΔG^\ddagger | System | Concentration (M) | ΔH^\ddagger | $-\Delta S^\ddagger$ | ΔG^\ddagger |
|---------------------|-------------------|---------------------|----------------------|---------------------|------------------------|-------------------|---------------------|----------------------|---------------------|
| Formic Acid & Water | 0.1 | 335.16 | 0.192 | 392.32 | Propionic acid & water | 0.1 | 345.88 | 0.333 | 445.03 |
| | 1 | 346.58 | 0.210 | 409.14 | | 1 | 41.33 | 0.366 | 520.51 |
| | 5 | 346.58 | 0.253 | 497.08 | | 6 | 452.68 | 0.497 | 600.81 |
| | 13 | 330.08 | 0.238 | 400.90 | | 8 | 459.96 | 0.487 | 607.29 |
| | 15 | 352.08 | 0.157 | 398.71 | 10 | 448.90 | 0.448 | 582.25 | |
| | | | | | 13 | 415.89 | 0.305 | 506.78 | |
| Acetic Acid & Water | 0.1 | 399.51 | 0.307 | 430.99 | Butyric Acid & water | 0.1 | 346.58 | 0.290 | 462.26 |
| | 1 | 356.48 | 0.321 | 452.09 | | 2 | 426.39 | 0.346 | 529.85 |
| | 5 | 348.45 | 0.574 | 567.24 | | 4 | 468.11 | 0.416 | 592.05 |
| | 8 | 410.04 | 0.327 | 509.56 | | 6 | 475.31 | 0.497 | 623.45 |
| | 10 | 419.39 | 0.432 | 548.05 | | 8 | 489.293 | 0.495 | 636.83 |
| | 12 | 443.51 | 0.465 | 582.203 | 9 | 484.07 | 0.406 | 605.10 | |
| | 15 | 431.25 | 0.436 | 565.47 | | | | | |

Units: $\Delta H^\ddagger, \Delta G^\ddagger = (\text{cal mol}^{-1})$ & $\Delta S^\ddagger = \text{cal K}^{-1} \text{mol}^{-1}$

The intermolecular association also contributes to these negative values. The ability of butyric acid to form stronger hydrogen bond with water is greater as compared to other acids and their sequence is as under:

Butyric acid > Propionic acid > Acetic acid > Formic acid

All the systems involved in our previous studies exhibited positive η^E and negative δV . The activation parameters for example δH^\ddagger , δH^\ddagger and δS^\ddagger are tabulated in Table-1. The values of δH^\ddagger are positive indicating that association and dipole-dipole interactions increase the values of η^E . The values of δH^\ddagger and δG^\ddagger [15-16] for the mixtures are positive for each binary system studied and increase

with increase in concentration, while for some these values decrease. The trend of decline start from 12M, 10M, and 8M of acetic, propionic and butyric acid respectively.

References

1. R.H. Ewell and H. Eyring, *J.Chem.Phys.*, **5**, 726 (1937).
2. H. Eyring, *J.Chem.Phys.*, **4**, 283 (1936).
3. M. Javid Iqbal, M. Saleem and M. Afzal, *Islamabad J.Sci.*, **3**, 21 (1976).
4. M. Afzal, *Pak. J.Sci.Ind.Res.*, **16**, 17 (1973).
6. M. Afzal, M. Saleem and M.T. Mahmood, *J.Chem.Eng.Data.*, **34**, 339 (1989).
7. L. Ubbelohde, *Ind.Eng.Chem.Anal.* **9**, 85 (1937).
8. H. Eyring and R.E. Powell *Ind.J.Chem.*, **33**, 8347 (1941).
9. J.A. Baker and F. Smith, *J.Chem.Phys.*, **22**, 375 (1954).
10. J.O.Hirschfelder, C.F. Curtis and R.B. Bird "Molecular Theory of Gases and Liquids"; John Wiley and Sons p. 253 (1954).
11. M. Afzal, Proceeding of conference on industrial uses of electrochemistry, p. 119 (1982).
12. E.A. Guggenheim, "Mixtures"; Oxford University Press p. 29 (1952).
13. R.J. Fort W.R. Moore, *Trans. Farady Soc.*, **62**, 1112 (1966).
14. M.J. Prolongo, R.M. Mosegosa and J. Hermonclcx, *J.Phys.Chem.*, **88**, 2163 (1984).
15. T.M. Reed and T.E. Taylor, *J.Phys.Chem.*, **63**, 58 (1959).
16. R. Meger, M. Meyer, J.Nertzler and A. Pcancnclcx, *J.Chem.Phys.*, **62**, 405 (1971).