Molar Excess Volumes

Molar excess volumes, $V^E$, for binary mixtures of non-electrolytes provide information\textsuperscript{1-5} that enable us not only to understand molecular interactions between the components of a mixture but also to convert experimental data at constant pressure to data at constant volume\textsuperscript{6-7}. Battino\textsuperscript{8} has made an extensive review of literature on this subject prior to 1970.
Molar excess volume, $V^E$, can be determined by any of the following methods:

1. **Density measurement method**
2. **Dilatometric method**
3. **Continuous dilution method**

**Density Measurement Method**

Molar excess volume, $V^E$, is determined from the densities of the pure components and that of mixtures. Densities are determined either by the conventional pycnometer or by vibrating tube densimeter. Density determination of either pure liquids or their mixtures by pycnometric method is subject to serious errors as mixtures of known composition are made outside the pycnometer; this, however, can be minimized by applying the correction for buoyancy, displacement of the vapour of first component on addition of the second; and the density of the vapour in the space above the liquid.

**Dilatometer Method**

This is a convenient method of determining $V^E$ for binary and ternary mixtures of non-electrolytes. Besides, being a direct method, it requires fewer and less accurate weighings as compared to the density method. In this method the liquids are kept separated by a column of mercury and the change in volume on mixing the components is noted on a capillary graduated beforehand. The basic advantage of this
method is that the size of capillary can be varied according to the value of $V^E$. However, a minor disadvantage of the method is that the pressure on the liquids before and after mixing does not remain constant.

**Continuous Dilution Method**

Molar excess volumes can also be determined by continuous dilution dilatometer. In this dilatometer, liquids are progressively mixed in a closed system, except for capillary in which $V^E$ is measured by a change in mercury level. Further, mild degassing of the liquids are required.

A number of workers have determined molar excess volumes by utilizing various types of pycnometers for direct measurement of density. Garcia et al. have used Anton Paar densimeter for determination of the molar excess volumes of hexane and undecane mixtures at 288.15, 293.15, 303.15 and 308.15K.

Al-Azzawi and Awwad have measured $V^E$ at 303.15K for binary mixtures of ethylene glycol + diethylene glycol, + triethylene glycol and tetraethylene glycol + $\gamma$-butyrolactones from precise density measurements over the whole mole fraction range. $V^E$ is positive for ethylene glycol and diethylene glycol over whole mole fraction range. For tri and tetraethylene glycol $V^E$ curves are sigmoid with positive lobe at low mole fraction of glycol and negative at high. The results have been qualitatively interpreted in terms of several opposing effects.
Aggarwal and Sharma\textsuperscript{16} have determined $V^E$ of binary liquid mixtures of chlorobenzene (CB) + 2-octanol (2-OcOH) and THF + bromobenzene (BB) as function of composition by making sound velocity and density measurements. The results have been discussed in terms of molecular interaction between the component liquids and the same have further been supported by dielectric relaxation time and free energy of activation measured in these mixtures in dilute solution of benzene at a fixed microwave frequency.

Joshi et al.\textsuperscript{17} have determined molar excess volumes for binary mixtures of anisole with bromobenzene, + o-dichlorobenzene, + o-chloroaniline and 4p-dioxane from the results of density measurements at 298.15, 308.15, 308.15 and 313.15K over the entire range of composition. The negative values for anisole + o-chloroaniline have been attributed to specific interaction between the mixing components and the positive $V^E$ values for the remaining systems have been ascribed to dispersion type interactions.

The vibrating tube densimeter, however, provides a very quick and easy method to determine density of pure liquids and that of their mixtures\textsuperscript{18}. Many workers\textsuperscript{19-29} have determined $V^E$ data by employing vibrating tube densimeter.

Matos et al.\textsuperscript{30} have measured $V^E$ of eight binary systems formed of Pr of Bu formate with n-alkanes (from $C_6$
to C9) at 298.15K by vibrating tube densimeter and the same have been compared with those estimated using Nitta model.

Excess molar volumes, $V^E$ have been measured by Letcher et al.\textsuperscript{31} as functions of mole fraction $x$ at 298.15K and at atmospheric pressure for $[x(\text{isomer of } C_6 H_4(CH_3)2)] + [(1-x) C_k H_{k+1}OH]$ (where $k = 1, 2$ or 3) using vibrating tube densimeter. The results have been discussed in terms of relative position of methyl groups on benzene ring, the carbon chain length of an alkanol, and the excess partial molar volumes at infinite dilution.

Sandler and Palet\textsuperscript{32} have determined molar excess volumes of water + methanol, n-heptane + ethyl acetate, + n-butyraldehyde, and + isobutyraldehyde mixtures using a vibrating tube densimeter. Drabek and Cibulka\textsuperscript{33} have measured $V^E$ of binary mixtures of acetic acid and propionic acid with some homologues of alkanes at 298.15 and 308.15K, using a tilting dilution dilatometer. The excess volumes are positive over the entire concentration range for all mixtures and increase with increasing length of an alkane molecule; decrease with increasing length of the alkyl chain in a molecule of carboxylic acid, and increasing with increasing temperature.

Chandrasekhar et al.\textsuperscript{34} have measured $V^E$ for diethylamine and triethylamine with isomeric butanol at 303.15K by using batch type dilatometer. Increase in
branching result in decrease in H-bonding interactions with amine. Reddy and Rao\textsuperscript{35} have also determined $V^E$ of N, N-dimethyl formamide and N, N-dimethyl acetamide with aliphatic esters at 303.15K. Excess volumes are negative in all the systems over the entire range of composition. The results are discussed in terms of specific interactions between like and unlike molecules and the difference in size and shape of the component molecules.

Delgado et al.\textsuperscript{36} have studied the variation of the excess molar volume with temperature at 298.15 - 323.15K of binary mixtures of p-xylene + n-hexane, and + n-hexadecane mixtures. The experimental values of $\left( \frac{\partial V^E}{\partial T} \right)_P$ are negative for the system p-xylene+ n-hexane and positive for p-xylene+n-hexadecane mixtures.

Subramanyam Reddy and Jayalakshmi\textsuperscript{37} measured $V^E$ of binary mixtures of methylethylketone + benzene, + toluene, + chlorobenzene, + bromobenzene, and + nitrobenzene at 303.15 and 313.15K. The data are examined in terms of the original Flory (1965) theory. A sign agreement is found for the systems containing polar-polar components which fails in the case of polar-non polar systems. Flory's modified method predicts an agreement in size in $V^E$ and $H^E$ values for the benzene system.

Ramanjaneyulu et al.\textsuperscript{38} have measured $V^E$ for binary mixtures of tetrachloroethylene + hexane, +heptane, +
cyclohexane, + methylcyclohexane, + toluene, + bromobenzene, + chlorobenzene, and + nitrobenzene dilatometrically at 303.15K. The data have been interpreted in terms of (i) loss of dipolar association, difference in size and shape of molecules and (ii) specific interactions between unlike molecules.

Excess volumes, $V^E$, have been determined dilatometrically for 10 binary pyridine-alkanol mixtures by Dewan et al.\textsuperscript{39} over the whole composition range at 298.15K. The $V^E$ values are negative for pyridine-alkanol ($C_1$-C$_6$) mixtures, sigmoid for pyridine-heptanol mixtures (with negative $V^E$ values at lower mole fractions of pyridine) and positive for pyridine-alkanol ($C_8$-C$_{10}$) mixtures over the complete mole fraction range. $V^E$ values increased in a positive direction with increase in chain length of the alkanol ($C_1$-C$_{10}$). Experimental $V^E$ data have been analyzed in terms of graph theory which utilizes the concept of the third degree molecular connectivity index. The results obtained from graph theory were used to predict the association of pyridine and alkanols in the pure and mixed states. The $V^E$ data were also analyzed using the Prigogine-Flory-Patterson theory.

$V^E$ of $C_6F_6$ and $C_6H_5F$ + an octane isomer have been determined at 293.15 K by Reyes et al.\textsuperscript{40}. The equimolar values increase from 2,2,4-trimethylpentane to n-octane to

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\textsuperscript{39} Dewan, et al.

\textsuperscript{40} Reyes, et al.
cyclooctane. The results have been analyzed in terms of the generalized vander waals model and a semi-empirical equation of state. Stolypin and Mishustin\textsuperscript{41} have analyzed volumetric properties of THF-Pyridine mixtures in terms of McMillian-Meyer approach, which showed that all types of interactions can be described in terms of additive pair approximation.

Molar excess volumes for ternary mixtures of non-electrolytes, however, have not received as much attention as molar excess volumes for binary mixtures.

Singh and Sharma\textsuperscript{42} have measured excess volumes of some ternary mixtures of non-electrolytes, dilatometrically at 298.15 and 308.15K. The results have been analysed in terms of (i) Sanchez and Lacombe theory and (ii) an approach based on the mathematical discipline of graph theory.

Excess volumes of n-heptane + n-nonane + cyclohexane and n-heptane + n-decane + cyclohexane at 298.15K have been determined from density measurement by Garcia et al.\textsuperscript{43}. Various ways are compared for predicting the excess volumes of the ternary mixtures from experimental results for the binary mixtures.

Khanwalkar\textsuperscript{44} have determined excess volume of mixing $v_{ijk}^E$, excess isentropic compressibilities and excess free-energies of activation of flow for the ternary cyclo-hexane + CCl$_4$ + EtoAC system and the constituent
binary systems at 303.15K over a wide composition range. The results have been analyzed by using the procedure suggested by Rastogi, Nath and Das (1977) for $V_{ijk}^E$ and suggest that all the excess values can be fitted to the same analytical expression.

Boch and Miecznik\textsuperscript{45} have investigated volumetric and ultrasonic studies of ternary liquid solutions: Water-NMAA-NEAA. Excess molar volume, adiabatic compressibility of solution, excessive adiabatic compressibility and frequency have been calculated for water-N-methylacetamide-N-ethyl acetamide ternary solution at 283.15-313.15 K. The min. of the excess molar volume and adiabatic compressibility at \( \sim 0.4 \) mole fraction amide indicates that H-bonded molecular complexes \( 2X3H_2O \) are formed where \( X = \text{amide} \). Comparison of the behaviour of binary mixture solution $H_2O$-NMAA and $H_2O$-NEAA suggest that the existing interaction among molecules of NMAA and NEAA in ternary solution does not affect the composition of molecular complexes that are being formed.

Batch dilatometer for measurement of excess volumes of ternary mixtures and ternary volume effects in benzene-carbon tetrachloride-cyclohexane mixtures at 298.15K have been used by Lark et al.\textsuperscript{46}. Aracil et al.\textsuperscript{47} have measured vapour pressure and excess volumes of hexafluorobenzene-tetradecane and hexafluorobenzene-benzene-tetradecane
mixtures at 298.15K. The thermodynamic consistency of binary results have been checked by using a Pode approximation. The ability of several equations in correlating the ternary results have also been attempted.

Lark et al. have analyzed volume effects in acetone + carbon tetrachloride + cyclohexane and acetone + cyclohexane + chloroform mixtures. The differences between the experimentally determined $V^E$ values from the sum of the binary contributions, illustrated as equivalence contours are positive for the first system and both positive and negative for the second system.

Shukla et al. have extended Flory statistical theory to obtain a relation for the excess volume, considering a ternary liquid mixture to be made up of three binary mixtures. Excellent agreement between the experimental and theoretical excess volume (both in magnitude and sign) have been obtained.

A conventional non-electrolyte solution model which has led to successful predictive expressions for the thermomechanical properties of a solute in simple binary solvent mixtures have been extended by Acree and Tucker to ternary systems having AC and AC$_2$ molecular complexes. The general mixing model used assumes that the Gibbs free energy of mixing and excess volume can be separated into a chemical and physical contribution. The chemical interaction term
results from the formation of molecular-complexes and the physical contribution describes non-specific interactions between the uncomplexed and associated species in solution. Ten $A_{ij}$ (binary interaction) parameters are initially needed to describe all binary non-specific interactions present. By using simplifying approximations and mathematical manipulations, the number of binary interaction parameters is reduced to only three. Expressions derived from the general mixing model are used to estimate excess volumes of ternary acetone + cyclohexane + chloroform mixtures.

Limitations and applications of four popular expressions used by Acree and McCargar for predicting multicomponent thermodynamic properties from measured binary data have been re-examined using volumetric data for 37 ternary systems. All four methods provide very reasonable estimate of the ternary excess volumes. For computerized calculations and mathematical representation of experimental data, the BAB, Kohler and Jacob-Fitzner equations are preferred over the Redlich–Kister equation. The mathematical forms of the BAB, Kohler and Jacob-Fitzner equations are both symmetric and independent of the manner in which the properties of the three contributing binary systems are reported.

Bender et al. have measured molar excess enthalpies and molar excess volumes of the ternary
propylene-1-ol + triethylamine + n-heptane mixtures by flow calorimetry and the vibrating tube technique, respectively. Data of the three binary systems was also obtained. The excess properties are dominated by strong hydrogen bonds due to the self association of PrOH and the association of PrOH with TEA. The third component, heptane, serves mainly as an inert diluent. An extended version of the so called ERAS model has been used for describing $H^E$ and $V^E$ of the complete ternary system. The parameters adjusted to the binary data reveal that the hydrogen bonding enthalpies and volumes between PrOH and TEA are distinctly stronger than between self-associating PrOH molecules. In addition the widely applied NRTL model has also been used for describing $H^E$ of the ternary systems. $V^E$, however, cannot be calculated with the NRTL model.

**Molar Excess Enthalpies**

Molar excess enthalpies, $H^E$, for binary as well as ternary mixtures of non-electrolytes provides reliable information regarding the nature of interactions between the components of these mixtures. High exothermic enthalpy of mixing for binary mixtures, at low temperatures, have been interpreted by McGlashan and Morcom$^{53}$ and other workers$^{54-59}$ to indicate complexation between the unlike molecules of the mixture. On the other hand, endothermic enthalpies of mixing data have been interpreted generally in terms of the breakage of local bonds in the pure components.
Molar excess enthalpies, $H^E$, of binary and ternary mixtures can be determined by following methods:

i) From the temperature dependence of the excess free energy, derived from vapour pressure measurements at a series of temperatures.

ii) From direct calorimetric measurements by mixing process.

It has, however, been observed that reliable values of excess enthalpies cannot be obtained from excess free energy of mixing. The uncertainty in these vapour pressure derived $H^E$ values arises, firstly, due to small temperature range which forces one to compute small differences between large numbers and secondly, the necessity of making corrections for gas imperfections which are much larger (because of high vapour pressure at high temperature). The value of $H^E$ thus obtained are often inaccurate and cannot be relied upon. The direct calorimetric method (either an adiabatic or an isothermal), however, gives satisfactory results. In the adiabatic mode, the mixing vessel is kept in thermal isolation, and if $H^E$ is positive, a lowering of temperature takes place, and the fall in temperature on adiabatic mixing is nullified by simultaneous supply of heat. If the heat is supplied simultaneously, mixing is done under conditions which are more or less isothermal, and the correction factor for the exchange
of heat with the surrounding becomes very small. If $H^E$ is negative there is a rise in temperature of the mixture and this rise is measured. McGlashan has made extensive review of the subject and the different types of calorimeters used in determination of $H^E$ are discussed below.

Hirobe was the first to make $H^E$ measurement on binary liquid mixtures. In his experimental set up, the two components were separate by a thread of mercury in a V-shaped glass mixing vessel. A serious drawback of this calorimeter is that the liquids are always in contact with their vapour phase. This calorimeter was subsequently modified by Scatchard and Brown and Fock.

Kortum et al., Brown and Mathiesen described a mixing vessel in which one of the components was confined to a glass ampule immersed in a second liquid, and mixing was done by breaking the glass ampule with a stirrer. The vapour space in this calorimeter was very small. Vander Waals and Hermans described a metal mixing vessel in which the components were separated by means of a ground-in-stopper. The main shortcoming in all these calorimeters is that they have vapour phase in contact with the liquids which causes the evaporation of the liquids. Although some of the calorimeters discussed above have negligible vapour space, detectable error was found in the measured $H^E$ values.
An isothermal calorimeter was designed by Patterson et al.\textsuperscript{68} for measuring small molar excess enthalpies. This calorimeter did not have any vapour space and the to and fro motion of the mercury provided efficient mixing. Van Ness et al.\textsuperscript{69} designed a continuous dilution calorimeter to measure $H^E$ for binary mixtures of non-electrolytes. Coomber and Wormald\textsuperscript{70} designed a flow calorimeter incorporating a stirrer, for the measurement of molar excess enthalpies of binary liquid mixtures. The calorimeter was tested on benzene + cyclohexane mixtures. Elliott and Wormald\textsuperscript{71} have also designed a differential flow calorimeter for the measurement of molar excess enthalpies of benzene + cyclohexane mixtures at 298.15K and the results agree very well with the results of the best isothermal dilution calorimeter.

Hepler and Fenby\textsuperscript{72} have analysed their $H^E$ data for dimethylsulphoxide(i) + chloroform(j) mixtures in terms of physical (non-complexing) and chemical contributions to determine $K$ and $\Delta H_{ij}$ for the complexation $i+j \rightleftharpoons ij$ reaction. The equilibrium constant so determined compares well with those obtained from independent spectroscopic studies. A modification of this approach involving heat effects on dilution was utilized by Woycicki\textsuperscript{73} to show that there is a definite possibility of interaction between carbontetrachloride and $\pi$-electrons of the unsaturated hydrocarbon.
Further, as there is no universally accepted method to evaluate $h^E_{phys}$ for a mixture, Jambon and Philippe\textsuperscript{74} have suggested that $H^E$ data for 1,1,1-trichloroethane rather than carbon tetrachloride should be used to determine the magnitude of the 'non-specific' contribution to the properties of chloroform + proton acceptor mixtures.

Fenby and Hepler\textsuperscript{75} have further extended their approach to evaluate $K_{ij}$, $K_{ij_2}$, $\Delta H_{ij}$ and $\Delta H_{ij_2}$ for a binary (i+j) mixture in which both $ij$ and $ij_2$ molecular species are present. Singh et al.\textsuperscript{76} have also employed this approach to determine equilibrium constant and the enthalpy of formation of various molecular species in the complexation reaction $i_2+j \rightarrow ij+ij_2 + i_2j$ characterizing a binary $(i_2+j)$ mixture from the $H^E$ and $G^E$ data of $i_2+j$ mixtures at one temperature alone.

Arora et al.\textsuperscript{77} have determined molar excess enthalpies for cyclopentane + benzene, +carbon tetrachloride, +cyclohexane mixtures at 308.15K and for cyclohexane + carbon tetrachloride mixture at 298.15K and have examined their data for current theories of solutions and have shown that McGlashan's theory predict values for $H^E$ and $G^E$ that are in good agreement with their corresponding experimental values. Arora et al.\textsuperscript{78} have also measured molar excess enthalpies of aniline, o-toluidine and N,N-dimethylaniline with chloroform and have examined the results for molecular
interactions by Barker's theory. Their analysis has indicated that aniline and o-toluidine are associated through hydrogen bond. Barker's theory has also been employed to understand the magnitude and nature of various interactions between the components of these mixtures.  

Chao et al. have measured molar excess enthalpies, $H^E$, for methanol, ethanol, 1-propanol, 1-pentanol and 1-hexanol with MeEt ketone and Me iso-Bu ketone as functions of composition at 298.15K with a Picker flow microcalorimeter. For all the mixtures studied the $H^E$ values are positive over the entire composition range and increases in the order: methanol < ethanol < propanol < butanol < pentanol < hexanol. The results have been explained in terms of self-association of alkanol, dipole-dipole interaction and alkyl chain length of the ketones.  

Tomaszkiewicz et al. have presented the results of flow-calorimetric measurements of the heat of mixing in the methanol-water system at 278.15, 298.15 and 323.15K under pressure of 0.1, 20 and 39 mPa. The experimental results are correlated by using the Redlich-Kister, NRTL and UNIQUAC equations. The absolute values of the heats decreases with temperature and the extreme for each pressure shifts towards higher concentrations of MeOH.  

Nagata et al. have measured the excess molar enthalpies of chlorobenzene + methanol, + acetonitrile, and
+ ethanol, and of acetonitrile + chlorobenzene, + methanol, and + ethanol mixtures in an isothermal dilution calorimeter. An associated model has been used to correlate the binary observed results and to predict the ternary experimental results from binary parameters alone. Otin et al. have measured excess molar enthalpies, $H^E$, at 310.15K and 101.32mPa for the binary mixtures containing esters of fatty acids. The results show that $H^E$ of ester + n-hexadecane mixtures increases with decreasing chain length and with increasing unsaturation of the ester molecule.

Parashar et al. have measured enthalpies of mixing of binary mixtures of some aromatic amines with carbon tetrachloride and ethanol at 321.35K. Svejda and Siddiqi have measured $H^E$ of 2,2,2-trifluoroethanol + 2,5,8,11,14-pentaoxapentadecane by Picker calorimeter. Siimer and Kurvits have done calorimetric study of benzoic acid + cyclodextrin inclusion complexes at 313K using LKB flow calorimeter.

Sipowska et al. have measured $H^E$ for propane + propane-1-ol at 298.15, 323.15, 363.15 and 368.15K and at 5mPa and 15mPa. The results have been explained in terms of chemical, physical and structural effects and have been compared with UNIFAC-2 predictions. Sancho et al. have measured $H^E$ of pyrrole or furan or thiophene + benzene or cyclohexane and thiazole + benzene at 298.15K and 1,2
dimethylimidazole + benzene mixtures at 308.15K, with a quasi-isothermal calorimeter at atmospheric pressure in the absence of vapour phase. The experimental results have shown that excess enthalpies are positive over entire composition range, and are higher for cyclohexane than for benzene.

New high pressure flow calorimetric vessels have been designed by Jiang et al. With the vessels, heat of mixing can be measured from ambient temperature and pressure to 573K and 20mPa. Excess molar enthalpies of n-octanol-n-alkane and isopentanol-n-dodecane mixtures have been determined at 298.65K and 0.1 and 10mPa and they are positive over the entire mole fraction range for the four of these binary systems.

Pikkarainen has measured excess enthalpies of butane-1-ol or 2-methyl-propane-2-ol + formamide, + N-methylformamide, and + N-N-dimethylformamide mixtures with a flow microcalorimeter at 313.15K. The excess enthalpies are negative for 2-methylpropane-2-ol +N-methylformamide systems at low mole fractions of the amide and positive for the other mixtures. The results have been discussed in terms of molecular interactions in the mixtures especially those involving N-H-protons.

As in excess molar volumes, the excess molar enthalpies of ternary mixtures of non-electrolytes have also
not received much attention. A few investigators have, however, worked on ternary systems.

Nagata et al.\textsuperscript{93} have measured molar excess enthalpies at 298.15K of binary and ternary mixtures of methanol with acetone, chloroform, benzene and tetrachloromethane using an isothermal dilution calorimeter. The results have been analyzed using associated solution theory which includes four equilibrium constants for the self-association of methanol, and solvation equilibrium constant between unlike molecules.

Singh and Sharma\textsuperscript{94} have determined molar excess enthalpies, $H^E$, of the ternary mixtures CH$_2$Br$_2$(i) + benzene (j) or toluene (k), + o-xylene (k), and +p-xylene (k) calorimetrically at 298.15K. The data have been analyzed in terms of Sanchez and Lacombe theory and an approach based on graph theory. Singh and Sharma\textsuperscript{95} have also measured the heat of mixing of ternary mixtures containing methylene bromide, pyridine, cyclohexane, benzene, toluene, dichloroethane and or xylene calorimetrically as a function of temperature and composition. The data have been analysed in terms of Sanchez and Lacombe theory and "graph theoretical approach".

Lark et al.\textsuperscript{96} have measured excess enthalpies of 3 ternary mixtures consisting of benzene + CC$_4$ + cyclohexane at 303.15K, acetone + CC$_4$ + cyclohexane, and acetone +
cyclohexane + chloroform at 298.15K using an adiabatic calorimeter. Ternary effects determined as the differences of the experimental excess heats from those of the sum of the binary contributions by the Nissema method are positive for the first and second systems and both positive and negative for the last system.

Tamura and Nagata have used at 298.15K an isothermal dilution calorimeter to measure excess enthalpies for the ternary systems 1-propanol-acetonitrile-benzene and 2-propanol-acetonitrile-benzene and for the constituent binaries. The experimental data have been correlated by means of the association model of N and T (1985,1986) based upon mole fraction statistics.

Excess enthalpies of binary and ternary mixtures of acetonitrile with methanol, ethanol and benzene at 298.15K and 308.15K have been measured by Nagata and Tamura using an isothermal dilution calorimeter. The binary results are well reproduced with an association model which contains four equilibrium constants for the association of alcohols, two for that of acetonitrile and two solvation equilibrium constants between alcohols and acetonitrile molecules. The ternary results have been compared with those calculated from the model with binary parameters.

Excess enthalpy data for the ternary system methane-ethylene-carbondioxide have been determined
by Gagne et al. using a flow calorimeter. The binary interaction coefficients obtained for the binary systems have been used as initial values for the optimization procedure leading to the $k_{ij}$ for the ternary system. For the case of the ternary system studied in this investigation, 2 types of binary interaction coefficients $k_{ij}$ have been determined from experimental data, $k_{ij}$ is independent of temperature and pressure and $k_{ij}$ is a function of temperature and pressure. Experimental data have been compared with the prediction from Benedict-Webb-Rubin and Redlich-Kuong equations of data.

Zhon et al. have measured excess molar enthalpies at 298.15K by a flow microcalorimeter for the ternary cyclohexane + benzene + cyclohexanone and cyclohexane + toluene + cyclohexanone and also for the binary mixtures cyclohexane + cyclohexanone and benzene + cyclohexanone mixtures. Smooth representation of the data have been presented and are used to calculate constant excess enthalpy contours for the ternary systems. They have also measured and reported excess molar enthalpies of n-alkane + tetrachloromethane + benzene at 298.15K.
ION-EXCHANGE

The history of ion exchange can be traced back to Mosses\textsuperscript{101} for the softening of bitter water. With progressing industrialisation the focus subsequently shifted to plant-scale water softening, first with natural and later with synthetic inorganic ion exchanger\textsuperscript{102,103}. The next major evolution came in 1935 with the work of Adams and Holmes\textsuperscript{104} to invent ion exchange resin materials with many superior properties. Other important advances were the advent of more stable and reproducible ion exchange resin on styrene basis\textsuperscript{105} and of strong-base anion exchangers\textsuperscript{106} (with quaternary ammonium groups). Later important advances include the commercial development of effective inorganic ion exchangers in the form of synthetic zeolites\textsuperscript{107} ("molecular sieves" first synthesized by Barrer\textsuperscript{108}) and of macroporous ion exchange resins\textsuperscript{109,110}. The later opened up many applications under conditions, under which the active groups of conventional resins are not accessible for lack of swelling. Today, a wide array of improved organic and inorganic ion exchangers with a great variety of properties is available for laboratory-and plant-scale applications, ranging from chemical analysis to preparative separations, from catalysis to organic synthesis, from biomedical uses to decontamination and detoxification.
Ion exchange has contributed directly or indirectly to evolution and success of new disciplines in chemistry, engineering and biology. Teorell, Meyer, and Schlogly applied ion exchange in biophysics and biochemistry to the understanding of transport across living membranes. Much the same is true for dialysis apparatuses in biomedical engineering, such as the Kidney machines. Prediction and success of many techniques on enhanced oil recovery rely heavily on a correct understanding of ion exchange between reservoir fluids and clays and of adjustment of the ionic composition of injected fluids by ion exchange.

Ion exchange is principally a tool for chemical separations, and it is to this field that it has made some of its remarkable contributions—quite reasonable optical isomer separation are carried out without much ado. In ion exchange chromatography, with complexing agents, the same exchanger and same agent can produce either one or the other type of development, depending on concentration and pH of the agent. Instead of exploiting complex formation of ions with an agent in solution to accomplish effective separations, the complexing agent can be built into the ion exchanger so as to provide preference for ions which are most strongly complexed. This idea has been actively pursued and has led to a number of commercially available chelating resins widely used for special purposes.
The ligand exchange separations employing ion exchanger has widely been used for separation of amines, amino-acid etc. The extension of the ligand exchange idea, principally by Davankov\textsuperscript{115}, to equip resins with optically active centres and so achieve separations of optical isomers, and the generalization of the idea of "reactive ion exchange" by Janauer\textsuperscript{117}, who systematically combined ion exchange with reactions of many different types to achieve highly selective separations, particularly at trace level, and for protection of the environment are two principal examples that merit special attention.

One of the most important application of ion exchangers is as catalysts. The recognition that such ion-catalyzed reactions can be conducted in the ion exchangers instead of dissolved electrolytes as the catalyst sources\textsuperscript{118} dates back to the 1930's. Today, catalysts ion exchangers has gained special importance in key processes to manufacture automotive gasoline additives to provide effective no-knock performance in the absence of tetraethyl lead\textsuperscript{119} or with various types of synthetics fuels\textsuperscript{120}(e.g. "gasohol"). The largest scale application of ion exchange materials today is in the field of catalysis, but in a process for which the ability of the catalyst to act as ion exchanger is almost coincidental. Based on ideas somewhat
along these lines is another novel application of ion exchangers as disinfactants. Here resin are used that have high sorption affinity for bacteria and carry antibacterial agents such as quaternary ammonium ions as either functional groups or counter ions.

In order to gain a true appreciation of the role of ion exchanger in our present and future world we should reorient our thinking about ion exchange with more attention to its relation to polymers. As the present survey reveals that ion exchange has become too narrow a classification as many of the most fascinating and promising uses entail no exchange of ions. Rather, today, ion exchange as a field is polymers (organic or inorganic) with ionic or ionizable functional groups. In this context, then, actual ion exchange in the literal sense is only part of a larger, more interesting and more colourful picture, that of 'reactive' or 'functional' polymers, that is, polymers carrying groups capable of chemical reactions or of inducing such reactions. All the many applications of ion exchangers in operation other than ion exchange then have their logical place.

Some important ion-exchange studies in the recent past are as follows:
Kulkarni and Kulkarni have studied the sorption of n-Butylamine on Ferric-Exchanged Y-Zeolites. To the sorption of n-Butylamine (n-BA) on ferric exchanged Y-zeolite catalyst Freundlich equation is applicable. The amount of n-BA retained on zeolites under vacuum at different temperatures has been reported which predicts the trend in the acidic strength. FeNaY(46) Zeolite shows maximum number of strong acidic centres. The adsorption data for FeNaY Zeolite, activated at 500°C, shows migration of ferric ions from supercages to sodalite cages or hexagonal prisms, thereby lowering the acidity of zeolite. The isosteric heats of sorption of n-BA on FeNaY Zeolite have been determined, which support the heterogeneity of surface and migration of ferric-ion after heating at 500°C.

Ion-Exchange equilibrium studies of K⁺/Na⁺, Rb⁺/Na⁺ and Cs⁺/Na⁺ system on phosphonated toluene - phenol - formaldehyde cation exchange resin (Na⁺ form) has been made by Aboul-Magd et al. in pure water at different ionic strength (0.025, 0.05 and 0.1M) and at different pH values and activity coefficients of the ions have been obtained. The rational thermodynamic equilibrium constants have been found to be dependent on temperature and pH of the medium. Interestingly, the order of affinities at pH values 6.9 and 9.0 (Cs⁺ > Rb⁺ > K⁺ > Na⁺) is reversed at pH values 11.6 and 13.6. The thermodynamic functions ΔH°, ΔG° and ΔS° for
for the exchange reaction have been evaluated. The characteristics maximum water uptake of the resin in various ionic forms has also been calculated.

Studies on zirconium tungstate ion exchanger has been done by Sarkar and Basu. Granular Zirconium tungstate as an ion exchanger suitable for column operation has also been prepared. Distribution coefficients of several cations have been measured and a few separations of analytical importance achieved.

Janardana et al. studies on inorganic ion-exchangers include preparation, properties and applications of cerium (IV) vanadate. Cerium (IV) vanadate has been prepared by different methods by changing volume ratio, molarity and pH. Its ion-exchange capacity, chemical composition (Ce:V::1:4), chemical stability, distribution coefficients for 10-metal ions, and change in its capacity with ionic radii of incoming ion has been studied. The utility of cerium (IV) vanadate as an ion-exchanger has been tested by achieving some important binary and ternary separation such as Hg²⁺/Cd²⁺, Zn²⁺/Hg²⁺, Zn²⁺/Pb²⁺, Zn²⁺ - Hg²⁺ - Cd²⁺, Zn²⁺ - Pb²⁺ - Cd²⁺ and Mg²⁺ - Pb²⁺ - Cd²⁺.

Janardana and Nair have synthesized and characterised a new thermally stable inorganic ion exchanger, Cerium (IV) phosphomolybdate. The chemical composition (Ce: P:Mo::1:2:1), chemical stability, distribution coefficient, effect of temperature on ion exchange capacity and effect of
electrolyte concentration on distribution coefficients for metal certain/ions have been studied. The qualitative separation of Hg$^{2+}$/Pb$^{2+}$, Zn$^{2+}$/Pb$^{2+}$, Cu$^{2+}$/Pb$^{2+}$ and Mg$^{2+}$/Pb$^{2+}$ has been achieved on resin.

Changes in thermodynamic parameters in the exchange of alkaline earth metals with sodium ions in Dowex-50 Wx8 and Amberlyst-15 resins in aqueous medium have been carried by Toteja et al. 127.

The ion-exchange characteristic of Ca carbonates (calcite, aragonite, and vaterite) with Cd$^{2+}$ ion in aqueous solutions containing various counter-anions (Cl$^-$, NO$_3^-$ and CH$_3$ COO$^-$) have been studied by Nagasawa et al. 128 at 298.15K, using a normal batch method. The reaction characteristics are independent of the kind of counter-anions. The order of the reaction rates was vaterite $>$ aragonite $>$ calcite, and $\approx 80\%$ of Cd$^{2+}$ ion were taken up by aragonite and vaterite during long-time reactions. Although Cd$^{2+}$ ion in aqueous solutions were easily fixed as Cd carbonates and Ca soluted Cd carbonates with aragonite and vaterite, they were affected by calcite. The value of the molar ratios of Cd$^{2+}$/Ca$^{2+}$ were $\approx 1.0$ and 0.9 for aragonite and vaterite, respectively. The immobilization of Cd$^{2+}$ ion in aqueous solutions on Ca carbonates proceeds by lattice ion-exchange mechanism at room temperature.
Li⁺/H⁺, Na⁺/H⁺, Rb⁺/H⁺, K⁺/H⁺, Cs⁺/H⁺ exchange equilibria on a perfluorosulphonate exchanger (Nafion-117) have been investigated by Iyer et al. at 0.1 M ionic strength in aqueous medium, thermodynamic equilibrium constants of 0.78 to 12.6 (Li⁺/H⁺ to Cs⁺/H⁺) have been evaluated and the alkali metal selectivity sequence has been found to be Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺. The various ionic form of Nafion-117 involved have also been subjected to isopiestic water vapour sorption investigations and the hydration number and swelling free energies determined. The exchange selectivity have been found to be consistent with the sequence of ionic hydration and swelling free energies; the exchange free energies showing a linear relationship with the difference in free energies of hydration of the exchanging ions as per Eisenman's model. The expanded selectivity as well as swelling free energy ranges observed in Nafion-117 compared to Dowex 50W type of resins have been interpreted in terms of hydrative and osmotic swelling behaviours of the two exchangers. Existence of a solvent shared ion pair in Nafion-117 i.e. $-\text{SO}_3^-(\text{H}_2\text{O})\text{Cs}^+$ observed in an earlier study has been supported by the present selectivity data.

Mohapatra et al. have carried out separation of Co(II)-Zn(II), Co(II)-Mn(II) and Zn(II)-Mn(II) systems sulphate from their aqueous solutions through supported liquid membrane (SLM) containing organo-phosphorus acid in kerosene
as extractant and the implication of these data in hydrometallurgy have been briefly discussed.

Four gel type cation exchange resins have been prepared from the condensation product of maleic anhydride and p-aminobenzoic acid, i.e. 4-(2,5-dioxopyrrolin-yl) benzoic acid (DPBA): homopolymer of DPBA (A), copolymer with styrene (B), cross-linked polymer with divinyl benzene (DVB, 10 wt.%) (C) and condensation product of 4-amino-benzoic acid with poly (maleic anhydride-co-styrene) (D). The adsorption behaviour of these polymers has been investigated with different cations under various experimental condition by Patel et al.¹³¹.
REFERENCES


