

EXPERIMENTAL INVESTIGATION ON PHYSICO-CHEMICAL PROPERTIES OF SOME BINARY AND TERNARY LIQUID MIXTURES

Jeet Pal Singh

Research Scholar, Department of Chemistry, Narain (P.G) College Shikohabad, (U.P) , India

Arvind Kumar

*Associate Professor, Department of Chemistry,
Narain (P.G) College Shikohabad, Uttar Pradesh, India*

Abstract

Excess Volume for three binary mixtures viz. ethanol + [empty][EtSO₄], water +[empty][EtSO₄] and 1-propanol +[empty][EtSO₄] and ternary mixtures of ethanol + water +[empty][EtSO₄] at different mole fractions at temperature 298.15K

Key Words- Binary, Ternary, Ethanol, Propanol

Introduction

Knowledge of excess volume is very useful in predicting the behaviour of attraction forces in liquid mixtures. Excess volume of binary mixtures has been experimentally determined by various workers¹⁻³. But for many practical purposes it is necessary to predict the properties of multi component liquid mixtures from the properties of pure components and from the data of binary systems. More sophisticated treatment of the liquid mixture is given by the refined version of the cell model of Prigogine⁴ which requires various parameters for computational purpose showing poor agreement with the experiment. As far as our knowledge is concerned, very few planned investigations have been carried out on multi component liquid mixtures⁵⁻⁸. In most of the theories, properties of the multicomponent system are determined with the help of the properties of their binaries⁹⁻¹⁰ but only Flory's statistical

theory¹¹⁻¹² can be successfully utilized to predict the properties of the multi component system from those of the pure components. Most of the work on excess volume for binary systems has been carried out by Cibulka et al.¹³, Van and Patterson¹⁴ Costas and Patterson¹⁵, Zhang and Benson¹⁶, Barreiros et al.¹⁷.

Ionic liquids (ILs) are room temperature molten salts with unusual properties, such as their very low vapor pressures. This and other properties, such as their ability to solubilize an enormous variety of compounds, good thermal stability which make them liquid over a large temperature range including ambient temperature, nonflammability, and facility to recycle, make the ILs a new alternative of solvents for different processes. To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties including viscosity and density. The most studied ILs are those containing ammonium and imidazolium cations. Nevertheless, there are few investigations on ILs containing pyridinium cations¹⁸. In this work, we report excess volume of mixture of the ionic liquid 1-ethyl 3-methylpyridinium ethylsulfate, [empy][EtSO₄], ethanol, water and 1-propanol. This is a relatively new ionic liquid, and little information about its physical properties is available in the literature. In the present work the experimental measurements of excess volume for three binary mixtures viz. ethanol + [empy][EtSO₄], water + [empy][EtSO₄] and 1-propanol + [empy][EtSO₄] and ternary mixtures of ethanol + water + [empy][EtSO₄] are shown at different mole fractions. All measurements have been carried out at temperature 298.15K

Experimental:

Bicapillarypyknometer, which is used for measuring densities of liquid mixture is described by Parker and Parker¹⁹. The pyknometer was calibrated at the desired temperature with the help of double distilled water. The pyknometer was kept immersed vertically in a thermostat maintained at $25^{\circ}\text{C} \pm 0.01^{\circ}\text{C}$ for about half an hour for each measurement. Accuracy in the density measurement was found to be ± 0.0004 .

Theoretical

Flory model

The first cell model of Prigogine et al.²⁰ for chain molecule liquids uses a dependence of the configurational energy on volume equivalent to the Lennard-Jones(6-12) energy distance relation²¹ i.e.

$$u(v) = -2v^{-2} + v^{-4} \quad (1)$$

All the more by and large for a (m,n) potential,

$$u = \frac{(-nv^{-m/3} + mv^{-n/3})}{(n-m)} \quad (2)$$

This prompts the accompanying condition of state as,

$$\frac{Pv}{T} = (1 - bv^{-1/3})^{-1} + \frac{mn}{3(m-n)}(v^{-n/3} - v^{-m/3}) \quad (3)$$

where b is a pressing component and equivalents to $(m/n)1/(n-m)$.

In this way, Prigogine and collaborators used the cell partition²⁰ function of Hirschfelder and Eyring and a dependence of configurational energy²² on volume propelled by the Lennard-Jones(m,n) potential between point centres.

Flory and colleagues have additionally utilized the partition function of Hirschfelder and Eyring in addition to the van der Waals vitality volume connection.

$$\tilde{u} = -\tilde{v}^{-1}$$

Formally at least this connection might be gotten from eq (2) by putting $m=3$, $n \rightarrow \infty$.

So as to stretch out relating state hypothesis to manage the surface strain, Patterson and Rastogi²³ utilized the reduced parameters as,

$$\sigma^* = k^{1/3} p^{*2/3} T^{*1/3} \quad (4)$$

Called the characteristic surface tension of the liquid

Here k is the Boltzmann steady, Patterson and Rastogi expanded the basic cell model hypothesis of the surface strain of round particles by Prigogine and Saraga²⁴ to the instance of chain atoms. A segment encounters an expansion in the configurational vitality equivalent to $-\tilde{M}(\tilde{u})(\tilde{v})$ because of the passing of a portion, M , of its closest neighbours at the surface while moving from the mass stage to the surface stage. It's most appropriate esteem ranges from 0.25 to 0.29. In the present case the estimation of M is taken as 0.29 all through computation. The cell segment capacity of a portion at the surface is expanded because of the loss of obliging closest neighbours in a single bearing, so that,

$$\frac{\phi_{surface}}{\phi_{Bulk}} = \frac{\tilde{v}^{1/3} - 0.5b}{(\tilde{v}^{1/3} - b)} \quad (5)$$

Here b is a packing fraction given by

$$b = \frac{m^{1/(n-m)}}{n}$$

and tends to unity when $n \rightarrow \infty$.

According to Prigogine and Sarag the reduced surface tension is given by,

$$\tilde{\sigma}(v)^{2/3} = -M \tilde{u}(v) - T \ln \frac{(\tilde{v}^{1/3} - 0.5b)}{(\tilde{v}^{1/3} - b)} \quad (6)$$

The surface energy and entropy are given by

$$\tilde{\sigma}_U = -M \tilde{u}(v); \quad \tilde{\sigma}_S = \ln \frac{(\tilde{v}^{1/3} - 0.5b)}{(\tilde{v}^{1/3} - b)} \quad (7)$$

The quantities T , $\tilde{\alpha}$ and $\tilde{\beta}_T$ are given as functions of $\tilde{v}$ by Patterson and Rastogi²³ for the different models. For example with the eq.(3) choice of (m,n) on Flory model, eq.(7) becomes,

$$\tilde{\sigma}(v) = M \tilde{v}^{5/3} - \frac{(\tilde{v}^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} \ln \frac{(\tilde{v}^{1/3} - 0.5)}{(\tilde{v}^{1/3} - 1)} \quad (8)$$

Flory's measurable hypothesis has no immediate connection with ultrasonic speed. In this way, the assessment of ultrasonic speed of ternary fluid mixture through Flory's statistical theory requires the utilization of surely understood and very much tried Auerbach connection which is communicated as ,

$$C = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \quad (9)$$

where C , σ and ρ signify the ultrasonic velocity, surface tension and density of ternary liquid mixture individually. This method has been developed recently to evaluate the sound velocity in pure liquids and liquid mixtures. The legitimacy of Auerbach connection has likewise been tried.

In this manner, based on Flory hypothesis, surface tension of ternary fluid blend is given by the articulation,

$$\sigma = \sigma^* \tilde{\sigma}(v) \quad (10)$$

The characteristic and reduced parameter engaged with the above condition of surface strain can be found from Flory hypothesis by the accompanying technique.

The intermolecular energy E_0 for the liquid is expressed by,

$$E_0 = \frac{NrS\eta}{2V} \quad (11)$$

where N is the number of molecules, V is the volume per segment, rS is the number of contact sites and η is a constant characterising the energy of interaction for a pair of neighbouring sites.

The reduced equation of state derived from the resulting partition function is given by ,

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \quad (12)$$

The reduced quantities $\tilde{P}, \tilde{V}$ and $\tilde{T}$ are given by

$$\tilde{P} = \frac{P}{P^*} = 2pv^* / S\eta \quad (13)$$

$$\tilde{T} = \frac{T}{T^*} = 2v^*ckT / S\eta \quad (14)$$

$$\tilde{v} = v / v^* = V / V^* \quad (15)$$

Thus

$$P^* = ckT^* / v^* \quad (16)$$

Where $V=rv$ is the molar volume. The isobar at zero pressure is

$$T^* = \frac{\tilde{v}^{4/3}}{\tilde{v}^{1/3} - 1} \quad (17)$$

From which

$$\tilde{v} = \left[\frac{\alpha T}{(3 + 3\alpha T)} + 1 \right]^3 \quad (18)$$

where α is the thermal expansion coefficient at $P=0$ (or without appreciable error at 1 atm.). The temperature derivative of eq. (12) at constant volume evaluated for $P=0$ gives

$$P^* = \frac{\alpha}{\beta_T} T_v^{\sim 2} = \gamma T_v^{\sim 2} \quad (19)$$

Where β_T and γ are the isothermal compressibility and the thermal pressure coefficient respectively. The quantities T^* , P^* and V^* can be computed from α , β_T and v as prescribed by eq. (14) to (19).

Excess volume have been calculated by using following well known expressions

$$V^E = V - (X_1 V_1 + X_2 V_2 + X_3 V_3) \quad (20)$$

Result and Discussion

The experimental and literature values of density of pure liquids are shown in table 1.1.

For binary mixture of ethanol + [empty][EtSO₄], density, excess volume (V^E), are given in table 1.2. A close perusal of the table reveals that the minimum and maximum excess volume are -0.709 and 0.000 respectively.

For binary mixture of water + [empty][EtSO₄], density, excess volume (V^E), are given in table 1.3. A close perusal of the table reveals that the minimum and maximum excess volume are -0.095 and 0.000 respectively.

For binary mixture of 1-propanol + [empty][EtSO₄], density, excess volume (V^E), are given in table 1.4. A close perusal of the table reveals that the minimum and maximum excess volume are -0.338 and 0.000 respectively.

For ternary mixture of ethanol+ water + [empty][EtSO₄], density, excess volume (V^E) are given in table 1.5. A close perusal of the table reveals that the minimum and maximum excess volume are -1.107 and -0.257 respectively.

Table 1.1 Densities, ρ of Pure Liquids at T= 298.15K

S.No.	Component Liquids	ρ_{Exp} (g. cc ⁻¹)	ρ_{Lit}^* (g. cc ⁻¹)
1	Ethanol	0.78546	0.7854
2	Water	0.99705	0.99705
3	1-Ethyl-3-methylpyridiniummethylsulfate [empty][EtSO ₄]	1.22226	-

4	1-Propanol	0.79960	0.79960
---	------------	---------	---------

***Ref.25**

Table 1.2 Densities, ρ , Excess Molar Volumes, V^E , of the Binary Mixture Ethanol (1) + [empty][EtSO4] (2) at T= 298.15 K

x_1	$\rho(\text{g} \cdot \text{cc}^{-1})$	$V^E_{(\text{cc})}$
0.0000	1.22226	0.000
0.0609	1.21493	-0.117
0.1108	1.20833	-0.200
0.2066	1.19393	-0.336
0.3083	1.17571	-0.460
0.4004	1.15573	-0.540
0.4998	1.12953	-0.620
0.6034	1.09496	-0.674
0.7034	1.05168	-0.709
0.8452	0.96167	-0.596

0.9389	0.87077	0.405
1.0000	0.78546	0.000

Table 1.3 Densities, ρ , Excess Molar Volumes, V^E , of the Binary Mixture Water (1) + [empty][EtSO4] (2) at T = 298.15 K

x_1	$\rho(\text{g. cc}^{-1})$	$V^E(\text{cc})$
0.0000	1.22226	0.000
0.0526	1.22169	-0.085
0.1412	1.22012	-0.161
0.2445	1.21780	-0.240
0.3233	1.21558	-0.296
0.4174	1.21221	-0.360
0.4972	1.20839	-0.402
0.5880	1.20253	-0.446
0.6975	1.19135	-0.465
0.7928	1.17405	-0.436

0.9005	1.12944	-0.250
0.9484	1.0862	-0.095
1.0000	0.9972	0.000

Table 1.4 Densities, ρ , Excess Molar Volumes, V^E , for the Binary System 1-Propanol (1) + [empty][EtSO4] (2) at T = 298.15

x_1	$\rho(\text{g. cc}^{-1})$	$V^E_{(\text{cc})}$
0.0000	1.22220	0.000
0.0863	1.20844	-0.089
0.1279	1.20122	-0.134
0.2201	1.18356	-0.215
0.3243	1.16024	-0.279
0.4177	1.13568	-0.317
0.5126	1.10618	-0.338
0.6093	1.06997	-0.328

0.7176	1.01990	-0.324
0.8240	0.95678	-0.304
0.8834	0.91304	-0.265
0.9658	0.83778	-0.144
1.0000	0.79950	0.000

Table 1.5 Densities, ρ , Excess Molar Volumes, V^E , for the Ternary Systems Ethanol (1) + Water (2) + [empty][EtSO4] (3) at T = 298.15 K

x_1	x_2	$\rho(\text{g. cc}^{-1})$	$V^E_{(\text{cc})}$
0.0559	0.9196	1.02817	-0.335
0.1155	0.8615	1.00618	-0.624
0.1918	0.7872	0.97826	-0.879
0.2634	0.7175	0.95224	-0.994
0.3432	0.6397	0.92623	-1.068
0.4352	0.5501	0.89992	-1.107
0.6720	0.3194	0.84395	-0.910
0.8189	0.1764	0.81607	-0.619
0.0658	0.8853	1.06050	-0.445
0.1401	0.8149	1.03049	-0.734

0.3049	0.6587	0.96677	-1.033
0.3952	0.5731	0.93603	-1.093
0.6019	0.3773	0.87548	-1.011
0.0466	0.9420	1.00625	-0.257

REFERENCES

1. S. L. Oswal and N. B. Patel, Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures of Acrylonitrile with Organic Solvents J. Chem. Eng. Data, **45**(2), 225-230 (2000).
2. V. Syamala, P. Venkateswarlu and K. Sivakumar, Excess Volumes, Speeds of Sound, Isentropic Compressibilities, and Viscosities of Binary Mixtures of Acetophenone with Chlorotoluenes and Nitrotoluenes at 303.15 K J. Chem. Eng. Data, **51**(3), 928-934 (2006).
3. J. George and N.V. Sastry, Densities, Excess Molar Volumes at T = (298.15 to 313.15) K, Speeds of Sound, Excess Isentropic Compressibilities, Relative Permittivities, and Deviations in Molar Polarizations at T = (298.15 and 308.15) K for Methyl Methacrylate + 2-Butoxyethanol or Dibutyl Ether + Benzene, Toluene, or p-Xylene J. Chem. Eng. Data, **49**(4), 1116-1126 (2004).

4. I. Prigogine, V. Mathot and A. Billmans, "The Molecular Theory of Solutions"(North-Holland, Amsterdam, 1957).
5. D. R. Massengil and R. C. Miller, Temperature dependence of excess volumes for simple liquid mixtures: N₂ + Ar, N₂ + Ar + CH₄J.Chem. Thermodyn.,**5**,207-217(1973).
6. W. Brostow and J. S. Sochinski, Prediction of thermodynamic properties of ternary liquid solutions including metal alloys, J.Mat. Sci., **10**,2134-2145(1975).
7. Y. Marcus, 'Introduction to Liquid State Chemistry', John Wiley & Sons Pub. Co. New Jersey, 854-858 (1978).
8. E. L. Heric and J. G. Brewer, Viscosity in three quaternary liquid nonelectrolyte systems, J. Chem. Eng. Data, **15**,379-382 (1970).
9. G. L. Bertrand, W. E. Acree, Jr. and T. E. Burchfield, Thermo chemical excess properties of multi component systems: Representation and estimation from binary mixing data, J. Soln. Chem., **12**(5), 327-346 (1983).
10. W. E. (Jr.) Acree and G. L. Bertrand, Thermo chemical investigations of nearly ideal binary solvents. (III) Solubility in systems of nonspecific interactions, J. Phys. Chem, **81**, 1170-1173 (1977).
11. P. J. Flory, Statistical thermodynamics of liquid mixtures, Am. Chem. Soc., 87, 1833-1838 (1965).
12. P.J. Flory and A. Abe, The thermodynamic properties of mixtures of small nonpolar molecules, J. Am. Chem. Soc., **87**, 1838-1846 (1965).
13. M. L. McGlashan ,I. Cibulka and M. B. Ewing $\{(1 - x)c\text{-C}_n\text{H}_{2n} + x\text{CCl}_4\}(\text{l})$ and $\{(1 - x)c\text{-C}_n\text{H}_{2n} + x\text{CHCl}_3\}(\text{l})$: excess molar enthalpies $H_m^E(E = 298.15 \text{ K}, x)$ for $n = 7$ and $n = 8$; and excess molar volumes $V_m^E(T = 298.15 \text{ K}, x)$ for $n = 7$, J. Chem. Thermodyn., **15**, 49-53 (1983).

14. H. T. Van and D. Patterson, Volumes of mixing and the P^* effect: Part (I). Hexane isomers with normal and branched hexadecane, *J. Soln. Chem.*, **11**, 793-805 (1982)
15. M. Costas and D. Patterson, Volumes of mixing and the P^* effect: Part II. Mixtures of alkenes with liquids of different internal pressures. *J. Soln. Chem.*, **11**, 807-821 (1982).
16. D. Zhang, G. C. Benson, Excess volumes of (n-decane + a hexane isomer) at 298.15 K, *J. Chem. Thermo.*, **18**, 619-622 (1986).
17. W.B. Streett, S. F. Barreiros, C.G. Caldo and M. N. Da Ponte, Thermodynamic properties of liquid mixtures of krypton + methane, *J. Chem. Soc. Faraday Trans. I*, **79**, 1869-1880 (1983).
18. Begon˜a Gonza˜lez,[†] Noelia Calvar,[†] Elena Go´mez,[†] Euge´nia A. Macedo,[‡] and A´ ngeles Domı´nguez*,[†] Synthesis and Physical Properties of 1-Ethyl 3-methylpyridinium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures, *J. Chem. Eng. Data*, **53**, 1824–1828 (2008).
19. H.C. Parker and E.W. Parker, Chloride solutions as determined with a new pycnometer, *J. Phys. Chem.* **29**, 130-137 (1924).
20. I. Prigogine, N. Trapperniers and V. Mathot, Statistical thermodynamics of r-mers and r-mer solutions, *Disc. Farad. Soc.*, **15**, 93-97 (1953).
21. J. E. Lennard-Jones and, A. F. Devonshire, critical phenomena in gases - I, *Proceedings of the royal society*, **163**, 53-70 (1937)
22. H. Eyring, and J. Hirschfelder, The theory of the liquid state, *J. Phys. Chem.*, **41** (2), 249–257 (1937)

- 23.** D. Patterson and A.K. Rastogi, The surface tension of polyatomic liquids and the principle of corresponding states, J. Phys. Chem., **74**, 1067-1071 (1970).
- 24.** I. Prigogine and L. Saraga, Test of monolayer model for surface tension of simple liquids, J. Chem. Phys., **49**, 399-407 (1952).
- 25.** Riddick, J.A., Bunger, W.B., Sakano, T.K., Technique of Chemical Organic Solvent; Physical Properties and Methods of Purification, IV Ed. John Willy & Sons, 1986