Critical Analysis of Thermodynamic and Transport Properties of Liquid and Liquid Mixture

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Abstract: *The study of thermodynamic characteristics of liquids and liquid mixtures is crucial to comprehending the nature of molecular interactions in the system. Excess thermodynamic characteristics in multicomponent fluid mixtures give important information on intermolecular interactions. For design calculations including separations, heat transfer, mass transfer, and fluid movement, understanding the thermodynamic and physical characteristics of multi-component systems is critical. The present paper represents the critical analysis of thermodynamic properties of fluids. Redlich-Kister approach and McAllister 3, 4 body models were employed to test the validity of the experimental findings.*

Keywords: *Density, velocity, fluid, thermodynamic, viscosity, surface tension.*

1. Introduction

The study of fluid thermophysical characteristics is important for understanding molecular interactions and for designing many industrial chemical processes that involve heat, mass, and fluid movement. Owing to interactions between the solute-solute, solvent-solvent, and solute-solvent2, as well as interstitial accommodation due to structural factors, the variations in thermodynamic and transport parameters are quite complicated. A quantifiable estimation of liquid mixtures is required to design the mass transfer operations.

More sophisticated treatments [3-4] of liquid mixtures derived their conceptual basis from-
(a) the cell model for liquids and (or) from –
(b) the postulations of a universal form for the intermolecular potential expressed by

$$\in_{ij} = \in^*_{ij} \phi(r_{ij} = r^*_{ij})$$

where, r_{ij} is the distance between centres of molecules i & j, $\in^*_{ij}$ & r^*_{ij} are characteristic parameter for the pair, and $\phi(r/r^*)$ is the universal function of its agreement.

The intermolecular energy is usually discussed on the basis of the familiar Lennard-Jones potential operating between the molecular centres. Even in comparatively simple polyatomic molecules, the acentric distribution of polarizable electrons necessitates fairly drastic modification of this potential. Kihara[3], Hamann and Lambert[4] and Pitzer[5,6] have offered modified intermolecular potentials for polyatomic (globular) molecules, especially those approximating spherical symmetry in form.

An extension [7] of these considerations which suggests itself, as a basis for treating the intermolecular energy in liquid consists in integrating the interactions of elements of the core of one molecule with the elements of all surrounding molecules, these latter being treated as occupying the space outside the cavity reserved for the molecule in questions.

The result obtained departs markedly from the form of the intermolecular energy according to the theory of Lennard-Jones and Devonshire.

2. Literature Review

Density and viscosity of saturated liquid dimethoxymethane were measured at various temperatures by J. Wu et al[1]. P. Jain and M. Singh[2] measured density, viscosity and excess properties of binary liquid mixtures of propylene with polar and non-polar solvents. G. Cruz-Reyes et a1[3] established a correlation of viscosities of pure gases and liquids with the use of significant structure theory. R. J. Martins[4] interpreted the viscosity of pure liquids at elevated pressures. L. T. Novok[5] proposed modeling of viscosity of liquid mixtures of polymer solvent systems. Calculations of viscosity of

ternary and quaternary liquid mixtures were carried out by several workers[6].

Excess Gibbs free energy model for calculating the viscosity of binary liquid mixtures is given by R. J. Martins et.al.[7]. Generic van der Waals equation of state, modified free volume theory of diffused viscosity of simple liquids were determined by, Laghaei et. al[8], J. Wu[9] experimentally determined the viscosity of saturated liquid dimethylether at elevated temperatures. Viscosity of the homologous series of n-(trans-4-n-alkyl cyclohexyl) isothioganate was studied by J. Jadzyn[10]. Excess molar enthalpies of dimethylcarbonate and (methanol, ethanol, 1- propanol) at various temperatures and pressures were studied by S. Li and H. Dong[11].

3. Methodology

3.1 Experimental Section

High purity and AR grade samples of acetonitrile, formamide, N-methyl acetamide, N, N-dimethyl formamide and N, N-dimethyl acetamide used in this experiment were obtained from Merck Co.Inc. Germany and purified by distillation in which the middle fraction was collected. The liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vaccum pump. The purity of each compound was checked by gas chromatography and the result indicated that the mole fraction purity was higher that 0.99. All the materials were used without further purification.

Table 1: Experimental and Literature Values of Refractive index of Pure Components at 298.15 k

Liquids	n	
	Exp	Lit*
Acetonitrile	1.3402	1.3416
Formamide	1.4370	1.4468
N- Methylacetamide (NMA)	1.4270	1.4294
N,N-Dimethylformamide (DMF)	1.4267	1.4282
N,N-Dimethylacetamide (DMA)	1.4342	1.4356

Apparatus and Procedure

Before each series of experiments, I calibrated the instrument at atmospheric pressure with doubly distilled water. The calibration was accepted if the measurements were within $\pm7.9x10^{-4}$ g.cm^{-3} of the published values. The densities of the pure components and their mixtures were measured with the bi-capillary pyknometer. The uncertainty in the density measurements was better than $\pm7.9x10^{-4}$ g.cm^{-3} and reproducible to $\pm5x10^{-4}$ g.cm^{-3}. The liquid mixtures were prepared by mass in a air tight stopped bottle using a electronic balance model SHIMADZUAX-200 accurate to within ±0.1 mg. The average uncertainty in the composition of the mixtures was estimated to be less than ±0.0001. All molar quantities were based on the IUPAC relative atomic mass table.

Refractive index for sodium D-line was measured using a thermostatically controlled Abbe refractometer (Agato 3T, Japan). Calibration of the instrument was performed with double distilled water. A minimum of three readings were taken for each composition and the average value was considered in all calculations. Refractive index data were accurate to ±0.0001units.

A Precise prediction of the thermodynamic properties of multicomponent systems depends largely on the extent of interactions involved in the liquid mixture. A good correlation between the theoretical and experimental values clearly points out towards the consideration of all the possible interactions present. The magnitude of deviations in properties gives the measure of various interactions which may be associated with a particular multi component system. Structural physics is related to the interactions involved in the multi component liquid systems. Nature and type of bonding associated with the structure can readily be studied through the study of interactions. Many workers have aimed to work on the deviations in properties to study the interactions. Therefore, percentage deviations between experimental and theoretical values have been calculated and the theoretically predicted results were examined in the light of average percentage deviation. This parameter was calculated using the following equation.

Mean percentage deviation (σ)

$$= \frac{1}{N} \sum_{i=1}^{N} \left[\left| Z_{i,\exp} - Z_{i,cal} \right| \times 100 / Z_{i,\exp} \right]$$

Where z is any measured and theoretically computed thermodynamic parameter and N is the total number of sets.

4. Result and Discussion

4.1 Evaluation of Absolute Ultrasonic Velocity And Acoustical Impedance

J.Glinski applied the additivity of the time of transmission of the acoustic signal with the volume fractions of the components derived by Natta and Baccaredda.

By applying above model to surface tension can be calculated as;

$$\sigma_{Calc} = \frac{\sigma_A \sigma_B \sigma_{AB}}{\phi_A \sigma_B \sigma_{AB} + \phi_B \sigma_A \sigma_{AB} + \phi_{AB} \sigma_A \sigma_B}$$

Where σ_{calc} is the calculated surface tension of a binary liquid mixture, ϕ_i is the volume fraction of ith component, σ_i is the surface tension of the pure i^{th} component.

Table 2: Comparison of Average Percentage Deviation (APD) of Viscosity obtained from Three Liquid Models at Various Temperatures.

293.15 K

Component Liquid	PFP	RS	Gelenski
Acetonitril + formamide	28.5	20.12	2.12
Acetonitrile+ N-methyl acetamide	24.6	24.0	0.51
Acetonitrile+ NN'-dimethyl formamide	20.1	7.7	0.42
Acetonitrile+ NN'-dimethyl acetamide	8.2	6.7	5.5

298.15 K

Acetonitril + formamide	30.6	26.8	1.40
Acetonitrile+ N-methyl acetamide	25.3	20.3	0.33
Acetonitrile+ NN'-dimethyl formamide	18.5	8.5	0.51
Acetonitrile+ NN'-dimethyl acetamide	20.3	13.5	0.66

303.15 K

Acetonitril + formamide	34.0	35.0	1.12
Acetonitrile+ N-methyl acetamide	20.3	1.08	0.34
Acetonitrile+ NN'-dimethyl formamide	19.6	8.66	2.2
Acetonitrile+ NN'-dimethyl acetamide	18.4	18.6	0.60

308.15 K

Acetonitril + formamide	33.3	39.0	0.96
Acetonitrile+ N-methyl acetamide	18.8	12.0	0.33
Acetonitrile+ NN'-dimethyl formamide	17.9	11.6	0.42
Acetonitrile+ NN'-dimethyl acetamide	11.3	22.4	0.62

313.15 K

Acetonitril + formamide	38.6	32.3	0.55
Acetonitrile+ N-methyl acetamide	15.3	16.6	0.88
Acetonitrile+ NN'-dimethyl formamide	16.5	13.3	4.27
Acetonitrile+ NN'-dimethyl acetamide	9.5	23.3	0.48

4.2 Evaluation of Absolute Surface Tension

The surface tension of multi component liquid mixture is often essential in design calculations involving interfaces mass transfer, heat transfer, separations and fluid flow. Surface tension is also very helpful in the study of foaming, interfacial energy, small scale roughness, force field, contact angle, capillary approximation, gradient field interfaces, adsorption, adsorbate molecular rotation, coking process, adhesion patterns, surfactant, molecular dynamics etc.

Table 3 presents the comparison of average percentage deviation (APD of Flory (PFP), Sanchez, Goldsack, Eberhart, Ramaswamy (RS) and Glinski (GLI) approaches for surface tensions. Values of mole fraction (x_1), density of the mixture (ρ), experimental and theoretical values of surface tensions obtained from six models PFP, Sanchez, goldsack, Eberhart, RS and GLI and their corresponding percentage deviations for acetonitriel+ formamide, acetonitrile + NMA, acetonitrile + DMF, acetonitrile +DMA over the whole composition range at four temperatures.

Table 3: Comparison of Average Percentage Deviation (APD) of Surface tension by Prigogine- Flory - Patterson (PFP), Ramaswamy and Anbnanthan (corrected) (RS), Glinski (GLI), Sanchez, Goldsack and Eberhart Models for Binary Liquid Mixtures at Various Temperatures

4.3 Evaluation of Dynamic Viscosity

The ultrasonic speed and thermodynamic data derived from it have been widely used for this purpose. Measurement of sound velocity offers a convenient method for determining certain thermodynamic properties of liquids not easily obtained by other means.

Table 4: Comparison of Average Percentage Deviation (APD) of Acostical impedance by Prigogine- Flory - Patterson (PFP) , Ramaswamy and Anbnanthan (corrected) (RS) and Glinski (GLI) Models for Binary Liquid Mixtures at Various Temperatures.

T (K)	K_{as}	σ_{ab} (dyne/cm^2)	average %Δ pfp	average %Δ rs	average %Δ gli	average %Δ Sanchez	average %Δ Goldsack	average %Δ Eberhart
Acetonitrile+Formamide								
293.15	0.00013	57.80	3.88	4.98	6.48	5.24	4.46	4.99
298.15	0.00010	57.90	4.05	2.40	9.80	8.11	7.17	2.40
303.15	0.00012	57.20	3.60	2.62	10.15	8.52	7.44	2.63
313.15	0.00011	26.90	24.24	29.60	12.82	9.57	16.84	29.61
Acetonitrile+NMA								
293.15	0.00014	33.90	9.60	7.90	7.33	6.66	8.25	7.89
298.15	0.00015	33.10	18.54	8.26	7.72	7.10	8.68	8.26
303.15	0.00016	32.80	10.76	1.10	1.10	8.97	10.53	10.09
313.15	0.00018	32.20	8.02	7.24	6.73	6.04	7.67	7.23
Acetonitrile+DMF								
293.15	0.00012	36.30	10.19	8.55	7.97	7.63	9.37	8.55
298.15	0.00012	35.90	9.20	8.53	8.01	7.69	9.53	8.52
303.15	0.00012	35.50	9.36	8.68	8.19	7.91	9.73	8.67
313.15	0.00013	35.30	9.66	8.32	7.87	7.58	9.38	8.31
293.15	0.00013	32.90	19.28	10.02	9.18	7.65	10.26	10.02
298.15	0.00014	32.10	19.14	10.81	9.93	8.52	11.10	10.81
303.15	0.00014	31.80	20.80	12.69	11.80	10.45	12.99	12.69
313.15	0.00014	31.20	21.41	10.89	9.98	9.45	11.18	10.89

T (K)	K_{as}	Z ab*10^{-6} (kg/m/s2)	Average %Δ pfp	Average %Δ rs	Average %Δ gli
acetonitrile+formamide					
293.15	0.00013	1.10	8.1394	5.5330	13.1624
298.15	0.0001	1.20	9.0987	7.2641	15.1652
303.15	0.00012	1.30	3.2136	1.2711	9.5315
308.15	0.00011	1.90	5.9473	4.1347	12.967
313.15	0.00011	1.88	3.9332	2.8316	12.0538
acetonitrile+NMA					
293.15	0.00014	1.14	2.5462	3.8102	3.273
298.15	0.00015	1.23	2.3310	4.8677	4.4203
303.15	0.00016	1.18	1.6484	1.1036	1.1036
308.15	0.00017	1.16	1.2542	3.8593	3.5434
313.15	0.00018	1.24	3.3318	2.3752	2.2873

5. Conclusion

Thermodynamics can be used as a tool to determine many volumetric properties. Factors such as temperature, pressure affect the thermodynamic and volumetric properties considerably. From the present experimentation of absolute ultrasonic velocity and impedance, it was revealed that with the increase of mole fraction, the values of viscosity decrease at all temperatures except in few places. The average percentage deviation of Gelenski model is considerably good as compared to Ramaswami and Anbananthan and Prigogine-Flory-Patterson (PFP) models for all the systems and at all the temperatures which indicate good fittings.

From the experimentation study of evaluation of absolute surface tension, very less percentage deviations in RS and GLI models indicate good fitting. It can also be observed that all other models i.e., Sanchez, Goldsack and Eberhart also produce good results, which again signify the utility and applicability of these models. And at last from the study of dynamic viscisity, considerable good results in Ramaswamy and Glinski models as compared to PFP model indicate good fitting.

Substantial amount of work has been carried out by several workers on sound velocity, surface tension, viscosity, refractive index and compressibility for binary and multi-phase liquid mixtures particularly for non-polar systems. But theoretical prediction of these properties and their applicability could not be made successfully due to scarcity of experimental data. In the proposed work measurements for these properties have been carried out at various temperatures for different polar binary liquid mixtures and different liquid models particularly Prigogine-Flory Patterson model and McAllister model are applied in order to study the interactions in the liquid mixture and also to test the validity of the McAllister model for such polar binary liquid mixtures comparison between theory and experiment would be treated as the success of a particular model.

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