



# DENSITIES, VISCOSITIES AND EXCESS THERMODYNAMIC PROPERTIES OF MONOMETHYL AMMONIUM CHLORIDE IN TETRAHYDROFURAN AND WATER MIXTURES AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

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## ABSTRACT

Densities and viscosities of pure solvent mixtures of tetrahydrofuran–water have been measured as a function of the composition of various concentrations (0.02, 0.04, 0.06 and 0.08 m) at 298, 303, 308, 313 and 318 K. The experimental data have been used to calculate excess thermodynamic parameters such as viscosity ( $\eta^E$ ), molar volume ( $V^E$ ), Gibb's free energy ( $\Delta G^{*E}$ ), enthalpy ( $\Delta H^{*E}$ ), entropy ( $\Delta S^{*E}$ ) and Grunberg's interaction parameter ( $d$ ). The excess property values were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures. Densities and viscosities of Monomethyl ammonium hydrochloride in tetrahydrofuran and water mixtures were also measured. The obtained results were then analysed by the Bresslau-Miller equation, Masson's equation and Jones-Dole equation.

**Key words:** Density, Viscosity, Thermodynamic excess properties.

## INTRODUCTION

Densities, viscosities and derived thermodynamic parameters are of considerable interest in understanding the intermolecular interactions in binary and ternary liquid mixtures<sup>1</sup>. The thermodynamic properties of multi-component liquid mixtures and their analysis are important in an industrial process. The mixing of different compounds gives rise to solutions that generally do not behave ideally. The deviations from ideality are expressed by many thermodynamic variables, particularly by excess or residual extensive properties. Excess thermodynamic properties of mixtures correspond to the difference between the

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actual value of an extensive property and the value it would have if the system behaved ideally, and thus are useful in the study of molecular interactions and arrangements. In particular, excess properties reflect the interactions that take place between (solute + solute), (solute + solvent) and (solvent + solvent) species. The present work provides data for the characterization of the molecular interactions between solvents and hydrochloric acid salt of primary amine.

The survey of literature reveals that extensive data have been reported for the thermodynamic and transport properties of binary aqueous electrolyte solutions, but relatively few measurements have been made on ternary and multicomponent electrolyte solutions. Therefore, one of the objectives of the theory of electrolyte solutions is to calculate various properties of multicomponent electrolyte solutions in terms of the properties of binary solutions, and much effort has been made in the literature to develop simple equations that can make full use of the available information on binary electrolyte solutions and provide sufficient accuracy for predicting the properties of multicomponent solutions.<sup>2-9</sup>

Keeping these important aspects in view, the measurements of density and viscosity for binary liquid (THF–H<sub>2</sub>O) mixtures and for ternary liquid mixtures of monomethyl ammonium hydrochloride with solvent binary mixtures of tetrahydrofuran–water at various temperatures have been undertaken.

## EXPERIMENTAL

Tetrahydrofuran and monomethyl ammonium chloride used were AR grade chemicals. These chemicals were used without further purification. The water used was double-distilled, deionised and filtered twice. The solvent mixtures (0 to 100% by weight) and solutions of various concentrations of electrolytes (0.02, 0.04, 0.06 and 0.08 m) were prepared by using digital electronic balance with an accuracy of  $\pm 0.1$  mg.

Densities of solutions were measured with the help of a pycnometer with a bulb of capacity 7.5 cc with an accuracy of  $\pm 0.0001$  g.

Viscosities were measured using a Cannon-Ubbelohde viscometer. A thoroughly cleaned and perfectly dried viscometer filled with liquid was placed vertically in a glass-sided water thermostat. An electronic digital stop-watch with readability of  $\pm 0.01$  s was used for the flow time measurements.

Various physical and thermodynamic parameters were calculated from the measured data as –

(i) Excess molar volume.

$$V^E = \frac{(M_1X_1 + M_2X_2)}{\rho_{12}} - \left( \frac{M_1X_1}{\rho_1} + \frac{M_2X_2}{\rho_2} \right)$$

where M, X and  $\rho$  are molecular weight, mole fraction and density respectively. 1, 2 and 12 refer to solute (THF), solvent (water) and solution, respectively.

(ii) Apparent excess viscosity

$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2$$

where x and  $\eta$  are mole fraction and viscosity and 1, 2 and 12 refer to solute, solvent and solution, respectively.

(iii) Excess Gibb's free energy

$$\Delta G^{*E} = RT [\ln \eta_{12} V_{12} - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)]$$

where R - gas constant, T – absolute temperature,  $\eta_{12}$  – viscosity of mixture,  $V_{12}$  – molar volume of mixture,  $x_1, x_2$  – mole fractions of first and second component,  $\eta_1, \eta_2$  – viscosities of first and second component,  $V_1, V_2$  – molar volume of first and second component.

(iv) Excess enthalpy

$$\Delta H^{*E} = -T^2 \partial \left( \frac{\Delta G^{*E}}{\partial T} \right)$$

(v) Excess entropy

$$\Delta S^{*E} = (\Delta H^{*E} - \Delta G^{*E})/T$$

(vi) Gruenberg Nissan interaction parameter

$$d = \frac{\ln \eta_{12} - x_1 \ln \eta_1 - x_2 \ln \eta_2}{x_1 x_2}$$

(vii) Masson's equation

$$\varphi_v = \varphi_v^{\circ} + S_v^* \sqrt{c}$$

where,  $\varphi_v$  is apparent molar volume,  $\varphi_v^{\circ}$  is apparent molar volume at infinite dilution,  $S_v^*$  is slope and  $C$  is molal concentration.

(viii) Jone's – Dole Equation

$$\frac{(\eta|\eta_0 - 1)}{\sqrt{C}} = A + B\sqrt{C}$$

where,  $\eta$  and  $\eta_0$  are viscosities of solution and solvent, respectively,  $A$  is intercept,  $B$  is slope and  $C$  is molal concentration.

## RESULTS AND DISCUSSION

The experimental values of density ( $\rho$ ) and viscosity ( $\eta$ ) for binary liquid systems (THF–H<sub>2</sub>O) and ternary liquid systems (THF–H<sub>2</sub>O–MMAH) at 298, 303, 308, 313 and 318 K were experimentally determined. The values of apparent excess viscosity ( $\Delta\eta$ ) and excess free volume ( $V^E$ ) have been represented graphically in Fig. 1 and 2. It is observed from magnitudes of excess viscosity parameter for the binary solvent mixtures at different temperatures that all the systems showed an initial increase in excess viscosities followed by decrease. In other words, the excess viscosity parameter when studied as a function of composition of binary solvent mixture exhibits a maximum at all temperatures.

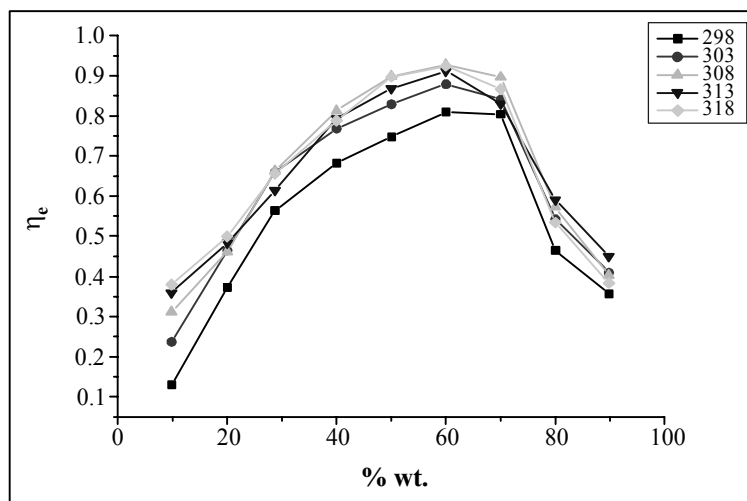
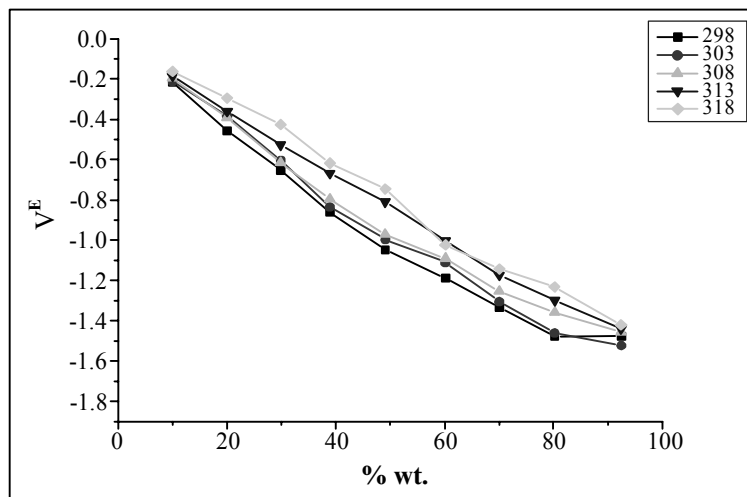


Fig. 1: Plot of  $\eta_e$  versus % by wt. of THF–Water



**Fig. 2: Plot of  $V^E$  versus % by wt. of THF-Water**

Excess volume is very much useful in understanding the strength and nature of interaction. Fig. 2 provides information regarding magnitudes of interaction for the systems studied at five different temperatures viz; 298, 303, 308, 313 and 318 K. Here a decrease in excess volume is observed which indicates strong attractive interaction.

Gruenberg Nissan interaction parameter ( $d$ ) values have been listed in Table 1. These values provide an index of strength of interactions between components of binary mixtures. In the present work, the magnitude of this parameter is positive indicating a strong specific interaction between the molecules.

**Table 1: Gruenberg Nissan interaction parameter ( $d$ )**

% by wt.	$d_{298}$	$d_{303}$	$d_{305}$	$d_{308}$	$d_{313}$
10	4.921	9.582	13.306	16.065	19.479
20	5.655	7.624	8.259	9.147	9.950
30	4.694	5.911	6.404	6.473	6.777
40	3.559	4.324	4.828	5.048	5.408
50	2.599	3.116	3.509	3.648	4.008
60	1.885	2.227	2.448	2.573	2.799
70	1.250	1.442	1.585	1.609	1.790
80	0.515	0.656	0.714	0.786	0.807
90	0.201	0.256	0.262	0.309	0.369

Excess Gibb's free energy ( $\Delta G^{*E}$ ), Excess enthalpy ( $\Delta H^{*E}$ ) and Excess entropy ( $\Delta S^{*E}$ ) have been shown in Table 2. These excess thermodynamic functions have been calculated from the viscosity and density data. Reed and Meyer considered excess free energy of activation as a reliable measure to detect the presence of interactions. Positive values of  $\Delta G^{*E}$  in our study of binary mixtures suggest strong specific interactions between the molecules forming molecular complexes. The values of  $\Delta H^{*E}$  are negative for all binary solvent mixture systems studied. The values of  $\Delta S^{*E}$  are negative suggesting that during flow process the structuredness occurs as a result of formation of activated complex.

**Table 2: Excess thermodynamic properties (kJ/mol) for THF–Water mixtures at different temperatures**

Temp.	298 K			303 K			308 K		
% by wt.	$\Delta G^{*E}$	$\Delta H^{*E}$	$\Delta S^{*E}$	$\Delta G^{*E}$	$\Delta H^{*E}$	$\Delta S^{*E}$	$\Delta G^{*E}$	$\Delta H^{*E}$	$\Delta S^{*E}$
10	1.99	-22.54	-0.08	1.43	-23.30	-0.08	0.98	-24.07	-0.08
20	10.08	-99.82	-0.37	9.56	-103.20	-0.37	7.10	-106.63	-0.37
30	14.96	-110.40	-0.42	14.81	-114.14	-0.43	13.48	-117.93	-0.43
40	18.39	-56.63	-0.25	18.21	-58.55	-0.25	17.99	-60.49	-0.25
50	21.52	-40.80	-0.21	21.34	-42.18	-0.21	21.65	-43.58	-0.21
60	25.36	-49.64	-0.25	25.08	-51.32	-0.25	25.19	-53.03	-0.25
70	29.31	-85.99	-0.39	28.23	-88.90	-0.39	28.58	-91.86	-0.39
80	21.85	-217.37	-0.80	20.24	-224.73	-0.81	19.05	-232.20	-0.82
90	14.09	-226.30	-0.81	7.52	-233.96	-0.80	0.91	-241.75	-0.79

Temp.	313 K			318 K		
% by wt.	$\Delta G^{*E}$	$\Delta H^{*E}$	$\Delta S^{*E}$	$\Delta G^{*E}$	$\Delta H^{*E}$	$\Delta S^{*E}$
10	0.67	-24.86	-0.08	0.51	-25.66	-0.08
20	6.01	-110.12	-0.37	3.78	-113.67	-0.37
30	11.01	-121.79	-0.42	8.26	-125.72	-0.42
40	16.82	-62.48	-0.25	15.57	-64.49	-0.25
50	20.44	-45.01	-0.21	20.12	-46.46	-0.21
60	24.18	-54.76	-0.25	23.50	-56.52	-0.25
70	25.70	-94.87	-0.39	25.34	-97.92	-0.39
80	16.78	-239.81	-0.82	5.95	-247.53	-0.80
90	0.10	-249.66	-0.80	-1.33	-257.70	-0.81

The densities of various solutions of Monomethyl ammonium chloride–THF–H<sub>2</sub>O justify the use of Masson's equation (eq viii) for the estimation of limiting apparent molar volume.

$$\varphi_v = \varphi_v^{\circ} + S_v^* \sqrt{c}$$

Where,  $\varphi_v^{\circ}$  and  $S_v^*$  are calculated from the intercept and slope from the extrapolation of the plots of  $\varphi_v$  against  $\sqrt{c}$ . The values of  $\varphi_v^{\circ}$  and  $S_v^*$  are recorded in Table 3. The slope  $S_v^*$  in Masson's equation may be attributed to be a measure of ion-ion or solute-solute interactions<sup>10-12</sup>. The low and positive values account for weak solute-solute interactions. There is an increase in inter-ionic interaction with increase in temperature which may be due to decrease in solvation of metal ions.

The  $\varphi_v^{\circ}$  is a measure of solute-solvent interactions. The decrease in  $\varphi_v^{\circ}$  values with increase in temperature may be due to extensive hydrogen bonding and thus making less free water molecules available for solvation and consequently solute-solvent interactions decrease with increase in temperature.

**Table 3: Computed parameters of masson equation for monomethyl ammonium chloride in THF–Water mixtures at different temperatures**

% wt.	$\varphi_{v298}^*$	$S_{v298}^*$	$\varphi_{v303}^*$	$S_{v303}^*$	$\varphi_{v308}^*$	$S_{v308}^*$	$\varphi_{v313}^*$	$S_{v313}^*$	$\varphi_{v318}^*$	$S_{v318}^*$
10	42.74	41.68	34.39	68.41	21.92	72.25	2.93	103.41	4.87	53.51
20	37.60	38.24	4.55	61.04	0.29	49.21	2.60	42.16	1.47	80.92
30	10.41	49.22	14.96	14.96	10.76	41.67	13.01	73.51	1.69	104.58
40	8.36	96.56	41.95	46.34	4.47	100.80	0.50	62.72	9.79	19.56
50	10.90	42.20	0.65	77.20	13.45	66.35	2.81	94.24	10.63	31.80
60	1.81	74.52	3.55	47.02	3.32	27.47	0.84	56.07	15.79	88.38
70	1.81	74.52	6.58	7.78	4.42	32.76	7.41	109.44	0.85	57.08
80	1.17	48.51	21.59	73.04	0.85	57.02	33.45	57.60	2.80	45.40

The viscosity data has been analysed on the basis of Jones-Dole equation. The values of A and B of different solutions at different temperatures have been recorded in Table 4.

**Table 4: A and B-coefficients of Jones-Dole equation for monomethyl ammonium chloride in THF–Water mixtures at different temperatures**

% wt.	A <sub>298</sub>	B <sub>298</sub>	A <sub>303</sub>	B <sub>303</sub>	A <sub>308</sub>	B <sub>308</sub>	A <sub>313</sub>	B <sub>313</sub>	A <sub>318</sub>	B <sub>318</sub>
10	0.0371	0.2624	0.0012	0.4179	0.0089	0.4803	0.0092	0.5862	0.0719	0.2820
20	0.0182	0.3592	0.0108	0.6821	0.4549	0.3848	0.4871	0.2832	0.4753	0.5709
30	0.0295	0.4147	0.0386	0.2292	0.1139	0.5873	0.3640	0.6330	0.6141	0.7159
40	0.0323	0.2453	0.0810	0.1966	0.1748	0.0564	0.2481	0.2437	0.3829	0.2579
50	0.0695	0.3524	0.0160	0.2912	0.0160	0.2912	0.1605	0.4328	0.1873	0.5133
60	0.0035	0.7202	0.0420	0.7472	0.0420	0.7472	0.0043	1.4981	0.1107	1.4769
70	0.0301	0.4137	0.1949	0.2469	0.1293	0.4527	0.4644	0.1228	0.4784	0.3256
80	0.4353	0.3406	0.4136	0.3380	0.2651	0.4090	0.2533	0.6095	0.7291	0.3763

Parameter A of Jones-Dole equation represents the contribution from solute-solute interactions. The ion-ion interactions increase with increase in temperature and composition of Monomethyl ammonium hydrochloride, which may be due to decrease in solvation of metal ions with increase in temperature and composition. The B parameter, which measures the structure making or breaking capacity of an electrolyte in a solution also contain a contribution from structural effects and is responsible for solute-solvent interactions in a solvent<sup>13</sup>. The positive B coefficient obtained may be due to large size ion.

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