

VISCOUS BEHAVIOUR OF METHOXY ETHANOL IN BINARY MIXTURES

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ABSTRACT

Viscosity and density of three binary mixtures of methoxyethanol with heptane, benzene and 1,4-dioxane have been measured at 308 K. the experimental data of viscosity were compared with theoretical values calculated by using various empirical relations. Further, the excess molar volume V^E , viscosity deviation $\Delta\eta$, excess viscosity $\Delta 1n\eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow have been calculated. The results are interpreted in terms of interactions.

Keywords: Viscous behaviour and methoxy ethanol.

INTRODUCTION

We have been engaged in the study of thermodynamic, acoustic and transport properties of liquid mixtures. In our previous investigations, we have reported viscosities, speed of sound, isentropic compressibilities and theoretical for various binary and ternary mixtures¹⁻⁴.

The nature of interactions in binary systems have been explained on the basis of certain thermodynamic properties such as excess volume, deviation in viscosity, deviation incompressibility, excess enthalpies etc.

Excess volume and excess thermal expansivities for binary mixtures of 2-methoxyethanol with n-octane, benzene and cyclohexane are reported by Ohji⁵. excess enthalpies, excess heat capacities, densities and cyclohexane were measured at different temperatures by Nishimoto *et al.*⁶.

In the present study, we have measured densities and viscosities of three binary mixtures of 2-methoxyethanol with heptane (I), benzene (II) and 1,4-dioxane (III) at 308 K.

EXPERIMENTAL

All the solvents used were fractionally distilled and their accuracy was checked by GLC. Further, viscosities and densities of these pure

solvents were measured which were in good agreement with literature values of Riddick *et al.*⁷.

Densities and viscosities of the three systems at various compositions were measured at 308 K by the procedures reported earlier. The uncertainty in the measurement of density and viscosity are $\pm 0.0001\text{g/ml}$ and $\pm 0.06\%$ respectively.

Theory

To evaluate the viscosities of binary liquid mixtures in terms of pure component data, various semi empirical relations have been proposed.

For binary liquid mixtures, Bingham relation⁸. Was modified to:

$$\eta = \sum x_i \eta_i \quad (1)$$

Additive relation based on Arrhenius and Eyring's model⁹ for the viscosity of pure liquids can be modified as:

$$\ln \eta V = \sum x_i \ln \eta_i V_i \quad (2)$$

Where x_i , η_i and V_i are the mole fraction, viscosity and volume of the i^{th} component respectively.

Hind *et al.*¹⁰ proposed the following equation:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_{12} \quad (3)$$

η_{12} is attributed to unlike pair interactions. It is approximately equal to 0.5 ($\eta_1 + \eta_2$) but this relation is not sufficiently accurate for the predication purpose. Equation (3) has been theoretically derived by Bearman and Jones¹¹ from statistical mechanical theory.

Kendall and Munroe¹² gave the following equation for multi component system,

$$\ln \eta = (x_1 \eta_1 + x_2 \eta_2) \quad (4)$$

The Grunberg and Nissam relation¹³ for the viscosity of non-ideal mixture is given by:

$$\ln \eta = \sum x_i \ln \eta_i + x_1 x_2 d \quad (5)$$

Where d is an approximate measure of strength of interaction between the components of the mixture.

$$d = -(\alpha F_m / x_1 x_2 RT) \quad (6)$$

where αF_m is the excess free energy of mixing and is given by

$$\alpha F_m = -RT(\ln \eta - \ln \eta_{\text{Bing}}) \quad (7)$$

where η_{exp} is the experimental viscosity value and η_{Bing} is the viscosity calculated by eq. (1).

The Katti and Chaudhari relation^{14,15} can be written as:

$$\ln \eta V = \sum x_i \ln \eta_i V_i + (W_{\text{vis}} / RT) x_1 x_2 \quad (8)$$

where W_{vis} is the interaction energy parameter among the components and is given by:

$$W_{\text{vis}} = (RT/x_1 x_2) \ln (V / \sum V_i x_i) + d RT \quad (9)$$

V is the volume of the mixture and V_i is the volume of pure components at different compositions.

RESULTS AND DISCUSSION

The theoretical values of viscosities and thermodynamic parameters like excess free energy of mixing, strength of interaction parameter and interaction energy etc are calculated from different equations mentioned above.

The experimental and theoretical viscosity values and thermodynamic parameters in the three

systems are given in Table - 1 for all the three system. The percentage deviations between experimental and theoretical viscosity values are given in Table - 2.

Table - 2 shows that in system 1, the deviation between experimental and theoretical values is large for almost all theories. In system II, good agreement between experimental and theoretical values is observed for Bingham relation. However, except Arrhenius relation, fair agreement is observed between experimental and theoretical values calculated. From other relations. In system III, very good agreement is observed for GN relation but except Arrhenius, all other theoretical values are in good agreement with the experimental results. The Arrhenius relation was proposed considering ideal mixing of solution, which is not true at all the composition of binary mixtures. Comparison of the three systems shows that in system III, which is methoxyethanol and 1,4-dioxane mixture, deviation is less in comparison to other two systems for all the theories.

In the mixture, quantitative estimation of interaction can be done by the strength of interaction parameter (d). The d values are generally negative except in system II, where it is positive for some compositions. It is reported⁷ that if d is greater than zero, weak interaction is present. Thus, weak interactions are present in system I and III, whereas in system II, interactions are somewhat stronger in comparison to other two systems.

Further, comparison of d values with αF_m shows that d values have opposite sign than that of αF_m . Values of αF_m are generally positive except for system II where it is negative for some compositions. A positive value indicates weak interaction whereas negative value suggests strong interaction in the mixture. This is further confirmed by W_{vis} values, which are highly positive for system II in comparison to other two systems, suggesting there by strong interaction in II system than in system I and III.

Thus, it may be concluded that all these relations can be used to calculate the viscosity of binary systems. However, Arrhenius relation does not give results due to non-ideal nature of selected binary systems. In methoxyethanol + benzene system, interactions are stronger than those in other two systems.

Table - 1 : Values of thermodynamic parameters and experimental and theoretical viscosities for the three systems

X_{Meth}	η_{exp}	η_{Bing}	η_{Ken}	η_{GN}	η_{Hint}	η_{KM}	η_{Arr}	D	αF_m	W_{vis}
I										
0.1028	0.4045	0.4863	0.4475	0.3748	0.4084	0.4575	0.5971	-1.9216	104.944	-1523.5
0.1966	0.4187	0.5652	0.4982	0.3690	0.4373	0.5170	0.6296	-1.8993	177.637	-784.4
0.3097	0.4444	0.6615	0.5669	0.3809	0.4994	0.5953	0.6712	-1.8605	235.520	-369.5
0.3965	0.4829	0.7354	0.6262	0.4112	0.5724	0.6605	0.7050	-1.7576	249.035	-104.6
0.5023	0.5763	0.8255	0.7068	0.4935	0.7019	0.7462	0.7485	-1.4373	212.757	-265.2
0.6045	0.6451	0.9125	0.7945	0.5617	0.8271	0.8356	0.7931	-1.4504	205.321	-347.0
0.6955	0.7914	0.9899	0.8817	0.7048	0.9764	0.9211	0.8349	-1.0569	132.547	-560.0
0.8013	0.8084	0.0800	0.9951	0.7449	1.0752	1.0752	0.8864	-1.8194	171.530	-103.5
0.9040	0.9156	0.1675	0.8935	0.8778	1.1835	1.1835	0.9394	-2.8002	143.893	-1985
II										
0.0563	0.5953	0.5726	0.5584	0.5806	0.5412	0.5623	0.5016	0.7328	-23.055	1616.45
0.1119	0.6167	0.6124	0.5855	0.5896	0.5580	0.5932	0.5222	0.0699	-4.112	1293.38
0.2208	0.6613	0.6905	0.6425	0.6153	0.6116	0.6568	0.5649	-0.2513	25.596	1242.28
0.3007	0.7094	0.7478	0.6879	0.6525	0.6716	0.7063	0.5985	-0.2507	31.216	1386.81
0.4048	0.7863	0.8224	0.7518	0.7187	0.7721	0.7744	0.6452	0.1865	26.609	1501.19
0.5292	0.9566	0.9116	0.8359	0.8772	0.9445	0.8614	0.7059	0.1932	-28.508	1761.76
0.6053	0.9757	0.9662	0.8920	0.9008	1.0068	0.9176	0.7458	0.0410	-5.793	1639.91
0.7019	0.0495	1.0355	0.9687	0.9818	1.1019	0.9926	0.7998	0.0644	-7.974	1575.95
0.7961	1.1684	1.1030	1.0497	1.1119	1.1932	1.0694	0.8566	0.3548	-34.105	1629.49
0.8881	1.2443	1.1690	1.1354	1.2086	1.2392	1.1482	0.9148	0.6284	-36.979	1624.12
III										
0.1029	0.9748	1.0278	1.0254	0.9725	0.9999	1.0261	0.8745	-0.5735	31.3468	504.66
0.1959	0.9884	1.0507	1.0466	0.9845	1.0075	1.0479	0.8860	-0.3883	36.2205	+314.17
0.3083	0.9903	1.0785	1.0728	0.9851	1.0207	1.0746	0.9001	-0.4000	50.5130	+657.27
0.3984	1.0012	1.1007	1.0943	0.9543	1.0410	1.0964	0.9116	-0.3954	56.1158	+809.38
0.5033	1.0168	1.1266	1.1198	1.0107	1.0721	1.1221	0.9251	-0.4102	60.7264	+870.84
0.6026	1.0467	1.1511	1.1447	1.0407	1.1133	1.1468	0.9381	-0.3972	56.3206	+843.14
0.6966	1.0965	1.1743	1.1685	1.0911	1.1691	1.1705	0.9505	-0.3244	40.6000	+753.78
0.8006	1.1757	1.2000	1.1955	1.1714	1.2159	1.1971	0.9645	-0.1281	12.1077	+564.54
0.9029	1.2557	1.2253	1.2228	1.2532	1.2480	1.2237	0.9785	+0.2802	-14.530	+5.7635

Table - 2: Comparison between the various viscosity data in the three systems

X_{ME}	$\Delta\eta_{ex-bin}\%$	$\Delta\eta_{ex-Ken}\%$	$\Delta\eta_{ex-GN}\%$	$\Delta\eta_{ex-Hi}\%$	$\Delta\eta_{ex-KM}\%$	$\Delta\eta_{ex-arrh}\%$
I						
0.1028	-19.38	-10.08	7.79	-0.19	-12.54	-46.88
0.1966	-34.99	-18.98	11.87	-4.44	-23.47	-50.37
0.3097	-48.85	-27.56	14.28	-12.37	-33.95	-51.03
0.3965	-52.29	-29.67	14.84	-18.53	-36.77	-45.99
0.5023	-43.24	-22.64	14.36	-21.79	-29.48	-29.88
0.6045	-41.45	-23.19	12.92	-28.21	-29.53	-22.94
0.6955	-25.08	-11.41	10.94	-23.37	-16.38	-5.49
0.8013	-33.59	-23.09	7.85	-33.00	-27.11	-9.64
0.9040	-27.51	+2.41	4.12	-29.25	-24.34	-2.59
II						
0.0563	3.81	6.19	2.46	9.08	5.54	15.73
0.1119	0.69	5.05	4.39	9.51	3.81	15.32
0.2208	-4.41	2.84	6.95	7.51	0.68	14.57
0.3007	-5.41	3.03	8.02	5.32	0.43	15.63
0.4048	-4.59	4.38	8.59	1.80	1.51	17.94
0.5292	4.70	12.61	8.30	1.26	9.95	26.20
0.6053	0.97	8.57	6.67	-3.18	5.95	23.56
0.7019	1.33	7.69	6.45	-4.99	5.42	23.79
0.7916	5.59	10.15	4.83	-2.12	8.47	26.73
0.8881	6.05	8.75	2.86	0.40	7.72	26.48
III						
0.1029	-5.43	-5.19	0.23	-2.57	-5.26	10.28
0.1959	-6.30	-5.88	0.39	-1.93	-6.01	10.36
0.3083	-8.90	-8.33	0.52	-3.06	-8.51	9.10
0.3984	-9.93	-9.29	4.68	-3.97	-9.50	8.94
0.5033	-10.79	-10.12	0.59	-5.43	-10.35	9.01
0.6026	-9.97	-9.36	0.57	-6.36	-9.56	10.37
0.6966	-7.09	-6.56	0.49	-5.96	-6.74	13.31
0.8006	-2.06	-1.68	0.36	-3.41	-1.82	17.96
0.9029	2.42	2.62	0.19	0.61	2.54	22.07

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