Excess Molar Volumes and Refractive Indices of Tetrahydrofuran, Dichloromethane, Trichloromethane, 1, 2-Dichloroethane, Trichloroethane and 1, 1, 2, 2-Tetrachloroethane

C. P. Gupta[1], Rajesh Singh[2], Ram Janam Gupta[3]

Chemistry Department, St. Andrew's College Gorakhpur -273001(India)

Abstract: ***Excess molar volumes V_m^E at T= 303 .15 k and refractive indices n at T= 298.15K have been measured for binary liquid mixtures of tetrahydrofuran (C_4H_8O) with dichloromethane (CH_2Cl_2), trichloromethane($CHCl_3$) , 1,2- dichloroethane (CH_2ClCH_2Cl), trichloroethane ($CH_2ClCHCl_2$) and 1,1,2,2-tetrachloroethane($CHCl_2CHCl_2$). The values of V_m^E have been found to be negative throughout the entire range of compositions for XC_4H_8O +(1-X) $CHCl_3$, XC_4H_8O +(1-X) $CHClCCl_2$, and XC_4H_8O +(1-X) $CHCl_2CHCl_2$. For XC_4H_8O +(1-X) CH_2Cl_2 the V_m^E have been found to be very slightly positive at very low values of molar fractions X of C_4H_8O , and negative at the higher values of X with inversion of sign of V_m^E occurring at X = 0.15. For XC_4H_8O +(1-X) CH_2ClCH_2Cl, the V_m^E has been found to be positive at lower values of X and negative at higher values of X , with inversion of sign of V_m^E occurring at X = 0.7. The values of V_m^E and n have been fitted with the representative equations. The V_m^E has been discussed in the light of the existence of electron donor- acceptor interaction between the components.***

Keywords: Excess molar volumes, Refractive indices, Mixture and tetrahydrofuran.

1. Introduction

This work continues the study programme devoted to mixture of n-donor component and chloroalkane, or chloroalkene. Such binary mixture is of considerable interest from the viewpoint of the existence of an electron donor-acceptor interaction between the components in the liquid state. In earlier work , Nath and Rashmi [1,2] have measured excess molar volumes V_m^E speed of sound (u) relative permittivities E_r and viscosities (n) of binary liquid mixture of 1,4-dioxane ($C_4H_8O_2$) and dichloroethane (CH_2Cl_2),or 1,2- dichloroethane (CH_2ClCH_2Cl) or trichloroethane ($CHClCCl_2$), or tetrachloroethane (CCl_2CCl_2),or cyclohexane (o - C_6H_{12}) at various temperature. Nath[3] has also measured the vapour pressures of this mixture. In addition Nath and Pandey [4] have measured V_m^E,and Nath[5] has measured u, for mixtures of $C_4H_8O_2$ and 1,1,2,2- tetrachloroethane ($CHCl_2CHCl_2$) at T=303.15k. This work reports the measurements of V_m^E at T=303.15K, and of refractive indices n_D at T=298.15K for binary liquid mixture of tetrahydrpfuran (C_4H_8O) and CH_2Cl_2 or trichloromethane ($CHCl_3$) or CH_2ClCH_2Cl or $CHClCCl_2$ or $CHCl_2CHCl_2$ and interprets the data obtained. Since organic liquid mixture are encountered in variety of areas and detailed studies about their mixing behavior is important from both practical and fundamental point of view , the results reported here in appear pertinent.

2. Experimental

HPLC grade chemicals dichloromethane and 1,2-dichloroethane, both of stated minimum purity of 99.8% (GLC), uv spectral grade trichloroethane of stated minimum purity of 99.5% (GLC), AR grade 1,1,2,2-tetrachloroethane of stated minimum purity of 99% (GLC) were all obtained from Sisco Research Laboratories, Mumbai, India. CH_2Cl_2, $CH_2ClCH_2Cl_2$, and $CHClCHCl_2$ were used without further purification. Liquid $CHCl_2CHCl_2$ was washed with 10% potassium carbonate solution, dried over anhydrous calcium chloride and then distilled fractionally. HPLC grade tetrahydrofuran of stated minimum purity of 99.8% (GLC) and HPLC grade trichloromethane of stated minimum purity of 99.5% (GLC) were obtained from qualigens fine chemicals Mumbai, $C_4H_8O_2$ was used without further purification. Liquid $CHCl_3$ was shaken several times with distilled water to remove ethanol present as a stabilizer, dried over anhydrous calcium chloride, then distilled fractionally, and stored in dark colored bottle covered with black cloth.

The excess molar volumes, V_m^E were measured with an uncertainty of the order of ± 0.002 cm^3. $Mol,^{-1}$ using a two- limbed pyrex glass dilatometer that was similar to that used by Nath et al[6] amount of the two liquid components were confined separately over mercury in the absence of air spaces in the two limbs of the dilatometer, which was mounted on a stand and immersed in thermostat water bath, Temperature was controlled with an a constant of ± 0.001K. The mixture of the two liquids was achieved by rocking the cell back and forth through a definite angle, and the mercury levels in the capillary of the dilatometer were noted using a cathetometer with an accuracy of ± 0.001cm.

The refractive indices (sodium- D line) n_D were measured with an accuracy of ± 0.0002 units, using a thermostated Abbe (Carl Zeiss) refractometer.

3. Results and discussion

The values of V_m^E for the present mixture of C_4H_8O and CH_2Cl_2 or $CHCl_3$, or CH_2ClCH_2Cl or $CH_2ClCHCl_2$ or $CHCl_2CHCl_2$ at T= 303.15K are reported in table 1, whereas the values of the refractive indices n_D of these mixtures at T = 298.15K are reported in Table 2, where X refers to the mole fraction of C_4H_8O in the various mixture. X has an uncertainty of ± 0.0001. The present values of n_D of C_4H_8O, CH_2Cl_2 , $CHCl_3$, $CHClCHCl_2$, $CHCl_2CHCl_2$, and $CHCl_2CHCl_2$ are 1.4050, 1.4212, 1.4428, 1.4420, 1.4250 and1.4916 respectively at T = 298.15K, as compared with the corresponding values 1.40496, 1.42115,1.44293, 1.4421, 1.4748 and 1.49168 at T= 298.15K respectively for the various liquids in the same order, as reported by Riddick and Banger [8], and Timmermans [9] The experimental values of V_m^E for the various systems of C_4H_8O have been plotted against the mole fraction x of C_4H_8O in Fig. 1, and have been fitted by the method of least squares with a Radlich – Kister [10] type equation.

$$V = x\,(1\text{-}x) \sum A_J\,(2x - 1)^{J-1} \qquad (1)$$

The values of the coefficients A_J of Eq. 1 along with the standard deviations V_m^E for the various systems are given in Table 3.

The values of the refractive indices n_D for the various systems have been fitted by the method of least squares with the equation

$$n_D = \sum B_J X \qquad (2)$$

The values of the coefficients B_J of Eq. (2), along with the standard deviations (n_D) are given in Table 4.

The present data show that the values of V_m^E at T=303.15K are negative throughout the entire range of composition for X C_4H_8O +(1-X) $CHCl_3$, X C_4H_8O +(1-X) $CHClCCl_2$ and X C_4H_8O +(1-X) $CHCl_2CHCl_2$. For xC_4H_8O +(1-X) CH_2Cl_2 the V_m^E is found to be very slightly positive a low values of X , and negative at high X values with inversion of sign of V_m^E from positive to negative values occurring at X ≈ 0.15. Also for XC_4H_8O +(1-X) $CH_2ClCHCl$, the V_m^E is found to be positive at lower values of X, and very slightly negative at high values of X, with inversion of sign from positive to negative values occurring at V_m^E X ≈ 0.7. At X =0.5, the values of V system of C_4H_8O have the following various present sequences:

CH_2ClCH_2Cl > CH_2Cl_2 > $CHClCCl_2$ > $CHCl_3$ > $CHCl_2CHCl_2$

The values of V_m^E may be interpreted in terms of the strength of intermolecular interaction between the molecules of the compositions of a given system. The negative values of V_m^E for a given system are attributed to a closer approach of unlike molecules of a system, leading to reduction in volume of mixture .The different types of forces that can exist between the molecules of the components of given systems are dispersion forces and charge transfer, hydrogen bonding, dipole – dipole, and dipole- induced dipole interaction. Dispersion forces leads to attraction between the molecules, and the relative magnitudes of the 1-1,2-2,1-2 type interactions between the molecules of components 1 and 2of a mixture are important in determining the thermodynamic excess properties. If the components of a mixture do not differ greatly in shape and size, the dispersion forces should make positive contributions to V_m^E. However, the charge-transfer, hydrogen bonding, dipole- dipole and dipole-induced dipole interactions should normally lead to negative contributions to V_m^E. Dispersion forces exist between the components of all systems, and for a given system in which there is more than one type of interactions between the molecules of the components, the values of V would be due to the net result of the contributions of all types of interactions. The highly negative values of V_m^E for X C_4H_8O +(1-X) $CHCl_3$, X C_4H_8O +(1-X) $CHClCCl_2$ and X C_4H_8O +(1-X) $CHCl_2CHCl_2$ show that C_4H_8O forms strong intermolecular complexes with $CHCl_3$, $CHClCCl_2$, and $CHCl_2CHCl_2$ in the liquid state. The specific interaction leading to the formation of complexes of C_4H_8O with $CHCCl_3$, $CHClCCl_2$, and $CHCl_2CHCl_2$ in the liquid state may be visualized as being due to the formation of hydrogen bonding between the components on account of interaction of H atoms in $CHCl_3$, $CHClCCl_2$ and $CHCl_2CHCl_2$ with the lone –pair electrons on the oxygen atom of C_4H_8O, as it is know [11,12] that 1,4- dioxane ($C_4H_8O_2$) forms the complexes $C_4H_8O_2$. $CHCCl_3$ and $C_4H_8O_2$. 2$CHCCl_3$ with $CHCCl_3$ via the interaction of H atom of $CHCCl_3$ with lone – pair electrons on the oxygen atoms of $C_4H_8O_2$. There is all likelihood of the formation of the strong hydrogen bonding between the molecules of C_4H_8O and CH_2Cl_2, or CH_2ClCH_2Cl. The values of V_m^E which are slightly positive at low x values and slightly negative at high X values , do not support the viewpoint of the existence of the formation of strong complexes of C_4H_8O with CH_2Cl_2 and $CH_2ClCHCl$ in the liquid state . This may be thought of being due to the predominance of the contributions to V_m^E arising from non – specific interactions over those from specific interactions between the components of the systems X C_4H_8O +(1-X) CH_2Cl_2 and X C_4H_8O +(1-X) CH_2ClCH_2Cl.

4. List of Symbols

A_J == Coefficients of Redlich – Kister type equation fitting the values of V
AR == Analytical reagent
B_J == Coefficients of the equation fitting the values of n_D
ϵ_r == Relative permittivity
GLC == Gas liquid chromatography
HPLC == High performance liquid chromatography
n-donor == Lone – pair electron donor
n_D == Refractive index for sodium –D light
$\delta(n_D)$ == Standard deviation in n_D
η == Dynamic viscosity
T == Temperature
U == Speed of sound
UV == Ultraviolet
V^E_m == Excess molar volume
$\delta(V^E_m)$ == Standard deviation in V^E_m

5. Acknowledgements

The authors are thankful to the Head of the Chemistry Department, DDU Gorakhpur University, Gorakhpur and Principal of St. Andrew's College Gorakhpur, for providing laboratory facilities. Thanks are also due to the University Grants Commission, New Delhi, India, for financial support.

Table: 1 Experimental values of the excess molar volumes, V^E_m, For C_4H_8O + CH_2Cl_2, or $CHCl_3$, or CH_2ClCH_2Cl, or $CHClCCl_2$, or $CHCl_2CHCl_2$ at T= 303.15k

X	V^E_m ($cm^3.mol^{-1}$)	X	V^E_m ($cm^3.mol^{-1}$)	X	V^E_m ($cm^3.mol^{-1}$)	X	V^E_m ($cm^3.mol^{-1}$)
X C_4H_8O +(1- X) CH_2Cl_2							
0.0383	0.002	0.3461	-0.024	0.6015	-0062	0.5211	-0.053
0.0784	0.004	0.3851	-0.034	0.6649	-0.063	0.8929	-0.038
0.1147	0.005	0.4455	-0.042	0.7296	-0.060	0.9358	-0.025
0.2466	-0.010	0.4876	-0.049	0.7555	-0.059	0.9428	-0.019
0.2958	-0.017	0.5433	-0.058	0.7765	-0.059	0.9765	-0.009
XC_4H_8O +(1-X) $CHCl_3$							
0.0538	-0.105	0.2986	-0.352	0.5556	-0.375	0.8015	-0.226
0.0877	-0.160	0.3514	-0.377	0.6072	-0.0357	0.8518	-0.179
0.1463	-0.236	0.4262	-0.392	0.6651	-0.335	0.9050	-0.120
0.1970	-0.283	0.4605	-0.393	0.7110	-0.302	0.9602	-0.053
0.2510	--0.324	0.5100	-0.385	0.7501	-0.270	0.9785	-0.049
XC_4H_8O +(1-X) CH_2ClCH_2Cl							
0.0506	0.036	0.2917	0.087	0.5539	0.036	0.3162	-0.013
0.0892	0.054	0.3589	0.081	0.5947	0.021	0.3714	-0.015
0.1383	0.070	0.3901	0.070	0.6550	0.010	0.8952	-0.015
0.1926	0.083	0.4419	0.059	0.7192	-0.002	0.9563	-0.009
0.2633	0.085	0.4928	0.049	0.7635	-0.009		
XC_4H_8O +(1-X) $CHClCCl_2$							
0.0529	-0.097	0.3149	-0.341	0.5693	-0.376	0.8682	-0.205
0.1112	-0.178	0.3708	-0.361	0.6300	-0.367	0.8994	-0.164
0.1814	-0.258	0.4250	-0.374	0.7236	-0.329	0.9505	-0.092
0.2181	-0.285	0.4764	-0.380	0.7757	-0.297		
0.2603	-0.310	0.5256	-0.378	0.8312	-0.242		
XC_4H_8O +(1-X) $CHCl_2CHCl_2$							
0.0815	-0.156	0.3504	-0.538	0.6548	-0.583	08799	-0.276
0.1385	-0.254	0.4467	-0.610	0.7057	-0.541	0.9188	-0.198
0.1800	-0.324	0.5066	-0.621	0.7609	-0.470		
0.2503	-0.428	0.5589	-0.624	0.3077	-0.402		
0.2814	-0.470	0.6061	-0.613	0.8399	-0.348		

Table: 2 Experimental values of the refractive indices, n_D of (C_4H_8O + CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, $CHClCCl_2$, $CHCl_2CHCl_2$) at T= 298.15 K

X	n_D	X	n_D	X	n_D	X	n_D
XC_4H_8O +(1-X) CH_2Cl_2							
0.0856	1.4198	0.2934	1.4166	0.5330	1.4125	0.8044	1.4083
0.1188	1.4190	0.3479	1.4155	0.5855	1.4118	0.8523	1.4073
0.1707	1.4183	0.3883	1.4148	0.6357	1.4109		
0.2156	1.4176	0.4384	1.4140	0.6866	1.4100		
0.2527	1.4171	0.4835	1.4132	0.7449	1.4090		
XC_4H_8O +(1-X) $CHCl_3$							
0.1089	1.4392	0.3008	1.4325	0.5020	1.4252	0.7381	1.4153
0.1509	1.4379	0.3604	1.4304	0.5450	1.4237	0.7961	1.4130
0.2041	1.4360	0.3981	1.4289	0.6455	1.4192		
0.2550	1.4342	0.4473	1.4273	0.6929	1.4173		
XC_4H_8O +(1-X) CH_2ClCH_2Cl							
0.1091	1.4393	0.3370	1.4330	0.6008	1.4240	0.8834	1.4118
0.1405	1.4386	0.3873	1.4314	0.6355	1.4227		
0.2401	1.4360	0.4275	1.4300	0.6796	1.4208		
0.2905	1.4344	0.4898	1.4279	0.7909	1.4162		
XC_4H_8O +(1-X) $CHClCCl_2$							
0.1146	1.4689	0.3363	1.4570	0.5704	1.4408	0.8036	1.4222
0.1664	1.4664	0.3691	1.4546	0.6660	1.4336	0.8469	1.4134
0.2224	1.4634	0.4177	1.4514	0.7137	1.4298		
0.2686	1.4608	0.4724	1.4478	0.7576	1.4260		
XC_4H_8O +(1-X) $CHCl_2CHCl_2$							
0.0762	1.4875	0.3455	1.4702	0.6517	1.4445	0.9067	1.4166
0.1338	1.4844	0.4582	1.4618	0.6829	1.4415	0.9525	1.4112
0.2293	1.4784	0.5079	1.4576	0.7536	1.4340		
0.2444	1.4774	0.5440	1.4544	0.8257	1.4260		
0.3057	1.4734	0.6073	1.4486	0.8535	1.4228		

Table: 3 Values of the coefficients A j of equation-1 and the standard deviations δ (V^E_m) for (C_4H_8O + CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, $CHClCCl_2$, $CHCl_2CHCl_2$) at T= 303.15 K

System	**A_1 ($cm^3.mol^{-1}$)**	**A_2 ($cm^3.mol^{-1}$)**	**A_3 ($cm^3.mol^{-1}$)**	**A_4 ($cm^3.mol^{-1}$)**	**A_5 ($cm^3.mol^{-1}$)**
XC_4H_8O +(1-X) CH_2Cl_2	-O.19860	-0.27289	0.02878	0.00421	0.0016
XC_4H_8O +(1-X) $CHCl_3$	-1.54754	-0.24433	-0.21234	0.16915	0.0028
XC_4H_8O +(1-X) CH_2ClCH_2Cl	-0.18860	-0.48260	0.09279	-0.04958	0.0018
XC_4H_8O +(1-X) $CHClCCl_2$	-1.52172	-0.03423	-0.50145	0.04858	0.0024
XC_4H_8O +(1-X) $CHCl_2CHCl_2$	-2.49710	-0.33292	0.24320	0.04505	0.0025

Table 4: Values of the coefficients B_j of equation- 2 and the stander deviation δ n_D for C_4H_8O + CH_2Cl_2 , or $CHCl_3$ or CH_2ClCH_2Cl or $CHClCCl_2$ or $CHCl_2CHCl_2$ at T=298.15K

Systems	**B_1**	**B_2**	**B_3**	**δ n_D**
XC_4H_8O +(1-X) CH_2Cl_2	1.421126	-0.016191	-0.000067	0.00011
XC_4H_8O +(1-X) $CHCl_3$	1.442947	-0.033139	-0.005171	0.00023
XC_4H_8O +(1-X) CH_2ClCH_2Cl	1.441722	-0.019958	-0.016198	0.00027
XC_4H_8O +(1-X) $CHClCCl_2$	1.474834	-0.045979	-0.024085	0.00019
XC_4H_8O +(1-X) $CHCl_2CHCl_2$	1.491263	-0.046070	-0.039937	0.00019

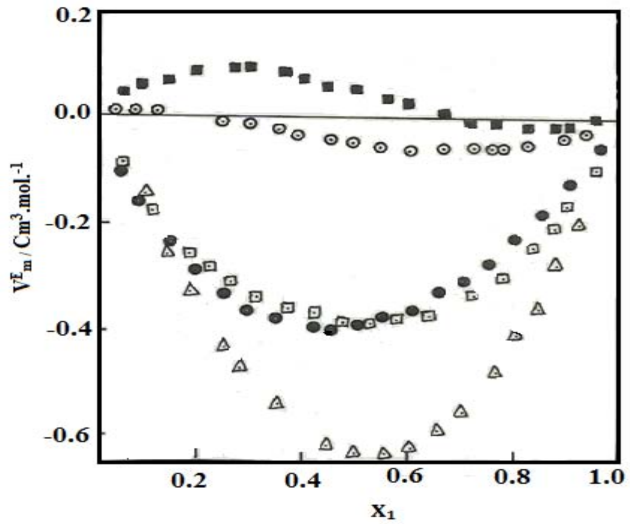

Fig. 1. Plot of Excess Molar Volume, Vm^E , against the mole fraction of C_4H_8O, X, for the following systems at T= 303.15K.

- ⊙ X_1 C_4H_8O + $(1-X_1)$ CH_2Cl_2
- ● X_1 C_4H_8O + $(1-X_1)$ $CHCl_3$
- ■ X_1 C_4H_8O + $(1-X_1)$ $C_2H_4Cl_2$
- ⊡ X_1 C_4H_8O + $(1-X_1)$ C_2HCl_3
- △ X_1 C_4H_8O + $(1-X_1)$ $C_2H_2Cl_4$

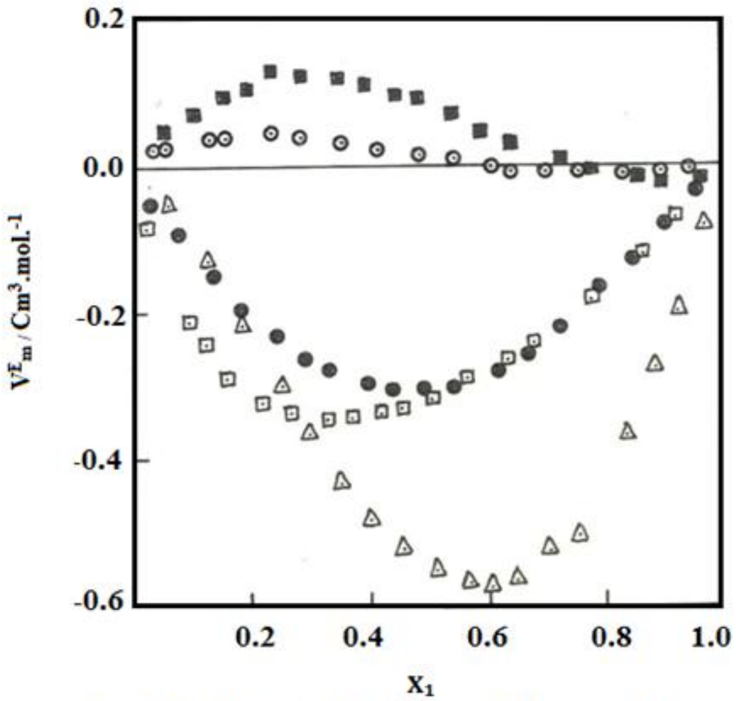

Fig. 2. Plot of Excess Molar Volume, Vm^E , against the mole fraction of C_4H_8O, X, for the following systems at T= 288.15K.

- ⊙ X_1 C_4H_8O + $(1-X_1)$ CH_2Cl_2
- ● X_1 C_4H_8O + $(1-X_1)$ $CHCl_3$
- ■ X_1 C_4H_8O + $(1-X_1)$ $C_2H_4Cl_2$
- ⊡ X_1 C_4H_8O + $(1-X_1)$ C_2HCl_3
- △ X_1 C_4H_8O + $(1-X_1)$ $C_2H_2Cl_4$

References

[1] Nath J. & Rashmi, Fluid Phase Equilibria 58 (1989) 319.
[2] Nath J. & Rashmi, J. Chem. Soc. Faraday Trans. 86 (1990) 3399.
[3] Nath J. Chem. Soc. Faraday Trans. 87 (1991) 1345.
[4] Nath J. & Panday J. G, J. Chem. Eng. Data 41 (1996) 844.
[5] Nath J.Chem. Thermodynamics 28(1996) 1083.
[6] Nath J. & Panday J. G, J. Chem. Eng. Data 42(1997) 514.
[7] Nath J. Mishra S. K., Fluid Phase Equilibria 152 (1998) 277.
[8] Riddick J. A.& Bunger W.B., Techniques of Chemistry , Vol.II, Organic Solvents: Physical Properties and Methods of Purification, 3rd edn, A. Weissberger: editor. Wiley- Inter Science, New York, 1970.
[9] Timmermans, J. Physico-Chemical Constant of Pure Organic Compounds, Elsevier, Amsterdam, 1950.
[10] Redlich O. & Kister A.T., J. Am. Chem. Soc. 71 (1949) 505.
[11] Mc.Glashan M. L. & Rastogi R.P, Trans Faraday Soc .54(1958) 496.
[12] Mc.Glashan M. L., Chemical Thermodynamics Academic Press, London, 1979.
[13] 13.Srivastava R., Jain A. K., Nath J. & Rashmi, Fluid Phase Equilibria, 58(1989) 319.