Molecular Interaction Studies on Binary Liquid Mixtures of 1,2-Dichlorobenzene and Toluene at 308.15k

S. P. Steevi Felixa, K. Uma Sivakami and A. Rose Venis
PG & Research Department of Chemistry, St. Joseph's College (Autonomous), Trichy

Introduction

Binary liquid solutions are the solution containing only two liquids. Both the liquids are supposed to be volatile, so in liquid solution the molecules are very close to each other. The thermodynamic properties of solvents such as density (ρ) and viscosity (η) are the two important physical properties of solvent system. These are used to explain the medium effect of solvent on transport phenomena. The nature of interaction in binary liquid mixtures of 1,2-dichlorobenzene and toluene from density and viscosity measurements at 308.15K.

When two or more liquids are mixed together, some changes in physical and thermodynamic properties[1,2]. Excess thermodynamic properties of mixtures are useful in the study of molecular interaction[3]. Thermodynamic para-meters derived from the measurement of density, viscosity are useful in understanding the nature and type of molecular interaction. From these values excess volume, excess viscosity and Gibb's free energy have been calculated with the Redlich-Kister type polynomial equation to estimate the interaction parameter and standard deviation[4,5].

The liquids were chosen in the present investigation on the basis of the industrial application.1,2-dichlorobenzene is an organic compound. It is used in softening and removing carbon base contamination on metal surfaces. Toluene is an organic solvent. It is widely used as an industrial feedstock.

Materials and Methods

1,2-dichlorobenzene and toluene were dried using suitable drying agents and distilled based on standard method[6,7]. Liquid mixtures of various concentrations were prepared by taking AR grade chemicals. Binary liquid mixtures of various compositions were prepared by mixing fixed amount of pure liquids in air tight stoppered bottles of 50mL capacity. The density of pure liquids and liquid mixtures were determined using a 10 ml relative density bottle. Viscosities were measured using Ostwald viscometer. All measurements were made with the help of digital thermostat at 308.15K.

Results and Discussion

The experimental densities ($\rho/kgm^{-3)}$ and viscosity ($\eta/kgm^{-1}s^{-1}$) for the pure liquids and binary mixtures are presented in Tables 1 and 2.

Table 1: Comparison of experimental densities (ρ) and viscosities (η) of pure liquids at T=308.15K with literature data

Liquid	Temp. (K)	Density(10^{-3} kg m^{-3})		Viscosity(cP)	
		Exp	Lit	Exp	Lit
1,2-dichlorobenzene	308.15	1.2875	1.2287	2.3168	2.3172
Toluene	308.15	0.8528	0.8528	2.6325	2.6431

Excess volumes (V^E) have been calculated by using the following relation[8].

$$V^E = (X_1M_1 + X_2M_2 / \rho_m)-(X_1M_1/\rho_1)-(X_2M_2/\rho_2) \quad ...(1)$$

where X_1,M_1 and X_2,M_2 are the mole fraction and molecular weight of component 1 and 2, ρ_1, ρ_2 are the densities of the pure liquid and ρ_m is the density of the liquid mixture.

Viscosities of pure liquid and liquid mixtures have been calculated using the following relation[2].

$$\eta = (At–B/t)\ \rho \quad ...(2)$$

where A and B are the characteristic constants of viscometer, 'ρ' the density of the liquid and 't' is the time of flow of the liquid.

The deviation in viscosity have been calculated by the following relation[9],

$$\Delta\ln\eta = \ln\eta_m-(X_1\ln\eta_1 + X_2\ln\eta_2) \quad ...(3)$$

where η_m is the viscosity of liquid mixtures and η_1 and η_2 are the viscosity of the pure liquids.

The Gibb's free energy G^{E*} of activation have been calculated by the following relation[10].

$$G^{E*} = RT\ [\ln\eta_m V_m-(X_1\ln\eta_1V_1 + X_2\ln\eta_2V_2)] \quad ...(4)$$

where 'R' is the gas constant, 'T' is the temperature, η_m is the viscosity of the mixture, V_m is the molar volume of the mixtures and $X_1\eta_1V_1$ and $X_2\eta_2V_2$ are the mole fractions and molar volume of the liquid mixture.

Calculated excess values were fitted to Redlich-Kister type polynomial equation[11].

$$\Delta A = X_1X_2\ [a+b\ (X_1–X_2) + c\ (X_1–X_2)] \quad ...(5)$$

By this method of least squares the adjustable parameters a,b,c were found out. From the a,b,c values theoretical values of all the excess parameters were calculated.

Standard deviation values were calculated using the following equation[12].

$$\Sigma = [(\Delta A\text{exp}-\Delta A\text{cal})^2/(n–m)]^{1/2} \quad ...(6)$$

where ‘n’ is the number of measurements and ‘m’ is the number of adjustable parameters.

Table 2: Density (ρ), Excess volume (V^E) and viscosity (η) for the binary liquid system of 1,2-dichlorobenzene and toluene at 308.15 K

S. No.	X_1	P (10^{-3} kg m^{-3})	V^E ($10^{-3}m^{-3}mol^{-1}$)	η (cP)	Δη (cP)	Δlnη (cP)	ΔG*E (KJ mol^{-1})
1.	0.0000	0.8528	0.0000	2.3176	0.0000	0.0000	0.0000
2.	0.8872	0.8656	0.1886	2.5828	0.2288	-0.7602	-92887
3.	0.7792	0.8743	0.2515	2.5727	0.1835	-0.7608	-92811
4.	0.6921	0.8833	0.3899	2.5628	0.1452	-0.6803	-92795
5.	0.5279	0.9067	0.4507	2.5558	0.0847	-0.6686	-92751
6.	0.3886	0.9240	0.5243	2.1833	0.3310	-0.7353	-96055
7.	0.2546	0.9464	0.5238	2.5909	0.0307	-0.7577	-93102
8.	0.2071	0.9720	0.4106	2.5791	0.0034	-0.7891	-92968
9.	0.1508	0.9949	0.3115	2.5789	0.0047	-0.8298	-93171
10.	0.0724	1.0191	0.1021	2.6197	0.0001	-0.8977	-93141
11.	1.0000	1.2287	0.0000	2.6431	0.0000	0.0000	0.0000

Table 3: Values of a, b, c and standard deviation

Parameters	A	B	C	Σ
V^E	1.9834	-0.8327	0.3938	0.0005
η	0.7063	0.6921	0.0564	$4.40x10^{-5}$

The calculated excess volume values are positive over the entire mole fraction values. This may be due to the greater repulsion that occurs between the mixing liquids. The strong repulsive force is acting between –Cl--Cl– in 1,2-dichlorobenzene, due to the presence of electron cloud in the benzene ring and –Cl atom in 1,2-dichlorobenzene. But the excess volume values are low positive values, so it may cause low repulsive force exists between the liquids. The attraction occurs between the methyl group and the electron cloud present in methyl benzene, that is within the toluene molecule and also attraction exists between $–CH_3$ and –Cl atoms present in dichlorobenzene. The toluene is polar because of methyl group electron donating character. Through such attractive force exists repulsive force dominates which leads to positive excess volume values. The liquid mixtures contain two polar compounds which results in the formation of polar-polar type of repulsion which leads to the repulsive force existing in between the mixing liquids.

Conclusion

Density, viscosity and excess volumes of the binary mixture of 1,2-dichlorobenzene and toluene at various mole fractions at 308.15K have been

studied. It is found that there predominates the formation of polar-polar type of repulsion, which leads to repulsive force.

References

1. A. K. Nain, R. Sharma A. Ali and S. Gopal, *Int. J. Thermophy*., 31 (2010) 1073.
2. S. C. Bhakia and G. P. Dubey, *J. Mol. Liq*., 144 (2009) 163-171.
3. K. Narendra, C. H. Srinivasu, S. K. Fakruddin and P. Narayanamurthy, J. Chem. Thermodyn., 43 (2001) 1604-1611.
4. Sathyanarany Boodida, Ranjith-kumar, Bacha Savitha, Jyostha Tangada, & Sathyanarayana Nallai, *Ind. J. Chem*., 47A (2008) 66-70.
5. A. Rose Venis and X. Rosario Rajkumar, *J. Chem. Pham. Resh*., 3 (2) (2011) 878-885.
6. A. Wiessberger, E. Proskauer, S. Riddick and J. A.Toops, E. E., *Technique of Organic Chemistry*, Vol. VII Organic Solvents, Inter Science, New york,1955.
7. A. I. Vogel., *A Text Book of Practical Organic Chemistry*, Longmans, London, 1975, 163.
8. A. Rose Venis and X. Rosario Rajkumar, *Asian J. of Chem*., 24 (3) (2012) 1195-1198.
9. Saravanakumar and K. Kubendren, *J. Chem. Sci*., 2(A) (2012) 50-56.
10. K. Vasudha, D. Vijakumari, G. Yuvaraja and A. Krishnaiah, *J. Chem. Pharm. Resh.*, 3 (5) (2011) 108-115.
11. O. Redlich , A. T. Kister, *Ind. Eng. Chem*., 40 (1948) 345.
12. Shrikant S. Joshi and Tejraj M. Aminabhavi, *J. Chem. Eng. Data*., 35 (1990) 247-253.