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Excess Volumes of Binary Liquid Mixtures of Benzene and Carbon Tetrachloride with Cumene and Pseudocumene

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Densitites (ρ), visocisities (η) and ultrasonic velocities for binary liquid mixtures formed from benzene and carbon tetrachloride with cumene and psedocumene have been measured at two different temperatures 303.15 and 293.15 K. Excess volume of mixing (v^E), deviation of excess volume (Δv^E) from ideal mole fraction law and parameter (d) as a measure of strengh of interaction between components of binary mixtures have been calculated from the data of densities and viscosities. Excess volumes have been found to be negative and positive in sign for binary mixtrue of carbon tetrachloride with cumene and pseudocumene and carbon tetrachloride with benzene at entire mole-fraction range and at both temperatures 303.15 and 293.15 K. On the other hand, Δη were found to be negative for binary mixtures of carbon tetrachloride with cumene and pseudocumene except the binary mixture of carbon tetrachloride with benzene at entire mole fraction range and temperatures mentioned. Positive value of excess volumes for three mixtures (carbon tetrachloride with benzene, cumene and pseudocumene) show weak molecular interactions between components. However, the negative value of Δη for binary mixtures of carbon tetrachloride with cumene and pseudocunene show weak interactions between components. The experimental values of excess volumes of mixing (v^E) have been analyzed in the light of Flory's theory.

Key Words: Excess volumes, Deviation, Carbon tetrachloride, Molecular interaction, Flory's theory, Cumene and pseudocumene.

INTRODUCTION

In recent years the molecular interaction in varoius binary liquid mixtures by several authors[1-6] through, volumetric, viscometric and ultrasonic studies have got considerable importance in framing theoretical models as well as its applications in a number of branches of science. The present work deals with the study of excess volumes of binary liquid mixtures of benzene and carbon tetrachloride with cumene and pseudocumene at entire molecular range and at temperatures 303.15 and 293.15 K. The regular trend in variation of v^E and Δη for binary mixtures[7] has not been found in present case. Some of the mixtures show positive[8] sign while other show negative sign for both v^E and Δη wich shows the existence of some specific interactions[9,10] there in. Negative values of both v^E and Δη for carbon tetrachloride + cumene + pseudocumene counter balance their effects showing some weak specific interaction between unlike components. Excess volumes of mixing (v^E), may be calculated from density[11] measurements, have been compared with theoretical values calculated on the basis of Flory's theory[12,13].

EXPERIMENTAL

Carbon tetrachloride (A.R., B.D.H) was purified by vigorous shaking with dil. NaOH solution and then fractionally distilled over P_2O_5 and stored.

Benzene (A.R., B.D.H) was shaken with conc. H_2SO_4 to remove trace of thiophene present if any. It was then washed with 10 % Na_2CO_3 solution followed by distilled water till free from alkali. It was then dried over anhydrous $CaCl_2$, fractionally distilled over P_2O_5 and stored over Na-wire. Cumene (Fluka Chemika) and pseudocumene (Fluka Chemika) both were distilled thrice by fractional distillation process. The purities of different component liquids were verified by density measurement. Binary liquid mixtures of varying composition were prepared.

RESULTS AND DISCUSSION

Excess volumes (v^E) of binary liquid miexture of varying composition were calculated by using-relation

$$v^E = v^{obs} - v^{id} \quad (1)$$

where v^{obs} is the experimental value of volume of binary liquid mixture.

TABLE-1
EXPERIMENTAL VALUES OF EXCESS VOLUMES (v^E) OF BINARY MIXTURE (CUMENE + BENZENE) AT 303.15 AND 293.15 K

Mole fraction of cumene	Volume excess v^E (c.c. mol^{-1})	Deviation from quation (Δv^E) (from Table-5)
Temp. 303.15 K		
0.0900	0.043	+0.001
0.2008	0.082	+0.000
0.3048	0.106	+0.001
0.5100	0.113	-0.001
0.5500	0.109	-0.001
0.6008	0.105	+0.001
0.7081	0.085	+0.002
0.8005	0.061	+0.002
0.9151	0.025	-0.001
Temp. 293.15 K		
0.1008	0.052	+0.000
0.2405	0.101	+0.001
0.3100	0.115	+0.001
0.4300	0.126	+0.002
0.5150	0.120	-0.001
0.6008	0.110	-0.001
0.7215	0.085	-0.001
0.8005	0.065	+0.001

TABLE-2
EXPERIMENTAL VALUES OF EXCESS VOLUMES (v^E) OF BINARY MIXTURES (PSEUDOCUEMENE + BENZENE) AT 303.15 AND 293.15 K

Mole fraction of pseudocumene	Volume excess v^E (c.c. mol^{-1})	Deviation from quation (Δv^E) (from Table-5)
Temp. 303.15 K		
0.0958	0.125	+0.002
0.2008	0.235	-0.001
0.3516	0.337	+0.001
0.4590	0.355	+0.001
0.4900	0.322	+0.001
0.4900	0.322	-.001
0.7150	0.243	+0.001
0.8056	0.167	+0.001
0.9085	0.075	+0.002
Temp. 293.15 K		
0.2008	0.251	+0.002
0.3156	0.335	+0.001
0.4900	0.369	-0.003
0.6008	0.340	+0.002
0.7500	0.235	-0.001
0.8600	0.135	+0.002

$$v^{obs} = \frac{M_1x_1 + M_2x_2}{\rho} \quad (2)$$

where ρ is the density of binary liquid mixture of given composition measured. v^{id}refers to the value for ideal binary mixture.

$$v^{id} = x_1v_1^0 + x_2v_2^0 = \frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2} \quad (3)$$

where M_1 and M_2 are the molar masses[14,15], ρ_1 and ρ_2 are densities of component liquids in pure state as well as x_1 and x_2 are the mole fractions of first and second components in mixture.

TABLE-3
EXPERIMENTAL VALUES OF EXCESS VOLUMES (v^E) OF BINARY MIXTURES (CUMENE + CARBON TETRACHLORIDE) AT 303.15 AND 293.15 K

Mole fraction of cumene	Volume excess v^E (c.c. mol^{-1})	Deviation from quation (Δv^E) (from Table-5)
Temp. 303.15 K		
0.1501	0.006	+0.000
0.2008	0.007	+0.001
0.3016	0.004	+0.000
0.3800	0.001	+0.000
0.4500	-0.002	-0.001
0.5196	-0.004	+0.000
0.5300	-0.005	-0.001
0.6602	-0.010	-0.001
0.7050	-0.011	-0.001
0.8101	-0.010	+0.000
0.8504	-0.010	+0.000
Temp. 293.15 K		
0.1005	0.003	+0.000
0.1700	0.004	+0.001
0.2812	0.002	+0.001
0.3500	0.000	+0.000
0.4500	-0.003	+0.000
0.5550	-0.007	+0.001
0.6900	-0.014	+0.000
0.8405	-0.013	+0.001
0.8905	-0.012	+0.000

TABLE-4
EXPERIMENTAL VALUES OF EXCESS VOLUMES (v^E) OF BINARY MIXTURES (PSEUDOCUMENE + CARBON TETRACHLORIDE) AT 303.15 AND 293.15 K

Mole fraction of pseudocumene	Volume excess v^E (c.c. mol^{-1})	Deviation from quation (Δv^E) (from Table-5)
Temp. 303.15 K		
0.1005	0.036	-0.001
0.2108	0.078	+0.001
0.4500	0.134	-0.001
0.5056	0.144	+0.001
0.6001	0.146	+0.002
0.7514	0.114	-0.001
0.8700	0.070	-0.001
0.9100	0.050	+0.000
Temp. 293.15 K (from Table-6)		
0.1508	0.066	+0.001
0.2008	0.085	+0.001
0.3508	0.126	-0001
0.4500	0.144	+0.001
0.5052	0.147	-0.001
0.6100	0.148	+0.002
0.7512	0.120	+0.000
0.8609	0.077	-0.002

Thus,

$$v^E = \frac{M_1x_1 + M_2x_2}{\rho} + \left[\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right] \quad (4)$$

where v^E is the excess volume of mixing which can be obtained from following empirical equation derived by the method of least square using only three parameters[16].

$$v^E = x_1x_2[A + B(x_2 - x_2) + C(x_1 - x_2)^2] \quad (5)$$

where A, B and C are characteristic constants of first and second components. Tables 1-4 constants for binary mixtures as well as x_1 and x_2 are mole.

The quations given in Tables 5-7 have been obtained from the experimental values of excess volume of mixing (v^E) for binary liquid mixtures of cumene + benzene, pseudocumene + benzene, cumene + carbon tetrachloride and pseudocumene + carbon tetrachloride at different temperatures by the use of the method least square. These are given by the following equation[18,19].

$$v^E \text{ mol}^{-1}\text{c.c} = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)] \quad (6)$$

where x_1 represents the mole fraction of first component (cumene or pseudocumene) and $x_2$represents the mole fraction of second component (benzene or carbon tetrachloride). A, B and C are fitting constants of binary mixtures concerned, which have been obtained by the method of least squares. The values of these constants[20] vary from one binary mixture to other and from one temperature to other, can be seen in individual equation enlisted in Tables 5-7. The last column of these tables present the standard deviation ($\sigma\Delta v^E$) which has been calculated using the following equation.

$$\sigma\Delta v^E \text{mol}^{-1}\text{c.c} = \left[\frac{\Sigma(\Delta v^E)^2}{(m-n)}\right]^{1/2} \quad (7)$$

where Δv^E is deviation in the experimental values of excess volume from that calculated from eqn. 6 and 'm' is the number of observations as well as 'n' is the member of constants used in eqn. 6.

Equations recorded in Table-7 represent the general form for v^E of binary liquid mixture[21] (temp. T K). These equations recorded in the Tables 5-7 for binary systems under investigation fit satisfactorily the experimentally observed values of v^E. The last column of Table-7 gives the values of $\delta v^E/\delta T$ for equimolar binary mixture[22].

After analysis of the results so obtained it is found that positive values of excess volume of mixing have been found for binary liquid mixtures of cumene and pseudocumene with benzene at entire mole fraction range[23] and at all the temperatures *i.e.*, 293.15 and 303.15 K. On the other hand both positive and negative values of volume excess have been found for binary liquid mixtures of cumene and carbon tetrachloride at the temperatures 293.15 and 303.15 K. It can be seen that positive values are found at lower mole fraction range and negative values at higher mole fraction range of cumene. However, positive values of volume excess could be observed for binary mixture of carbon tetrachloride with pseudocumene at entire mole fraction range and at both the temperatures *i.e.*, 293.15 and 303.15 K.

The comparative plot[24] of excess volumes (v^E) for binary liquid mixtures[25-27] of pseudocumene and cumene with benzene and carbon tetrachloride, plotted in the Fig. 1, shows that the values of excess volume of mixing (v^E) are maximum at almost all mole fraction range for the binary liquid mixture of pseudocumene with benzene. The volume excess of equimolal mixtures of cumene and pseudocumene with benzene and carbon tetrachloride are 0.1155, 0.3528 and -0.0034 c.c. mol^{-1} at 303.15 K.

Conclusion

The experimental data of excess volumes of mixing (v^E) are reported for binary mixtures of cumene and pseudocumene with benzene and carbon tetrachloride over entire range of mole fractions at 303.15 and 293.15 K. Calculated excess volume of mixing (v^E) and its deviation (Δv^E) are fitted in Redlich Kister type polynomial equations. A slight positive and negative deviations are observed for both the investigated binary systems. The present investigation shows that excess volumes of mixing are in the order of: pseudocumene + benzene > pseudocumene + carbon tetrachloride > cumene + benzene > cumene + carbon tetrachloride.

TABLE-5
EQUATIONS FITTING THE DATA FOR EXCESS VOLUME OF MIXING (v^E/c.c. mol-1) TEMP. 303.15 K

System	Equation fitting the experimental data	Std. deviation ($6\Delta v^E$)
Cumene + benzene (x_1)	$v^E = x_1x_1[0.4621\text{-}0.1171(x_1 - x_2) - 0.0546(x_1 - x_2)^2]$	0.0015
Pseudocumene + benzene (x_1)	$v^E = x_1x_2[1.4112\text{-}0.3352(x_1 - x_2) - 0.3873(x_1 - x_2)^2]$	0.0016
Cumene + carbon tetrachloride (x_1)	$v^E = x_1x_2[-0.0137\text{-}0.0944(x_1 - x_2) - 0.0104(x_1 - x_2)^2]$	0.0007
Pseudocumene + carbon tetrachloride (x_2)	$v^E = x_1x_2[0.5634 + 0.1360(x_1 - x_2) - 0.0592(x_1 - x_2)^2]$	0.0014

TABLE-6
EQUATIONS FITTING THE DATA FOR EXCESS VOLUME OF MIXING (v^E/c.c. mol-1) TEMP. 293.15 K

System	Equation fitting the experimental data	Std. deviation ($6\Delta v^E$)
Cumene + benzene (x_1)	$v^E = x_1x_1[0.4911\text{-}0.1294(x_1 - x_2) - 0.0293(x_1 - x_2)^2]$	0.0014
Pseudocumene + benzene (x_1)	$v^E = x_1x_2[1.4836\text{-}0.2987(x_1 - x_2) - 0.3005(x_1 - x_2)^2]$	0.0027
Cumene + carbon tetrachloride (x_1)	$v^E = x_1x_2[-0.0226\text{-}0.0986(x_1 - x_2) - 0.0387(x_1 - x_2)^2]$	0.0008
Pseudocumene + carbon tetrachloride (x_2)	$v^E = x_1x_2[0.5913\text{-}0.1074(x_1 - x_2) - 0.0065(x_1 - x_2)^2]$	0.0016

TABLE-7
EQUATIONS FITTING THE DATA FOR EXCESS VOLUME OF MIXING (v^E/c.c. mol-1) TEMP. T K

System	Equation fitting the experimental data	Dv^E/Dt
Cumene + benzene (x_1)	$v^E = x_1x_1[1.3414\text{-}0.0030t + (-0.4901 + 0.00124T)(x_1 - x_2) + (0.7123\text{-}0.00253(x_1 - x_2)^2]$	-0.00075
Pseudocumene + benzene (x_1)	$v^E = x_1x_1[(3.6064\text{-}0.00725T) + (-0.7710\text{-}0.00366T)(x_1 - x_2) + (2.2439\text{-}0.00865T(x_1 - x_2)^2]$	-0.00181
Cumene + carbon tetrachloride (x_1)	$v^E = x_1x_1[(-0.2829+0.000889T)+(0.22190.00043T)(x_1 - x_2) + (-0.8680+0.00285T(x_1 - x_2)^2]$	0.00022
Pseudocumene + carbon tetrachloride (x_2)	$v^E = x_1x_1[(1.4090\text{-}0.00278T)+(0.7309+0.00284T)(x_1 - x_2) + (1.5385\text{-}0.00530T(x_1 - x_2)^2]$	-0.00069

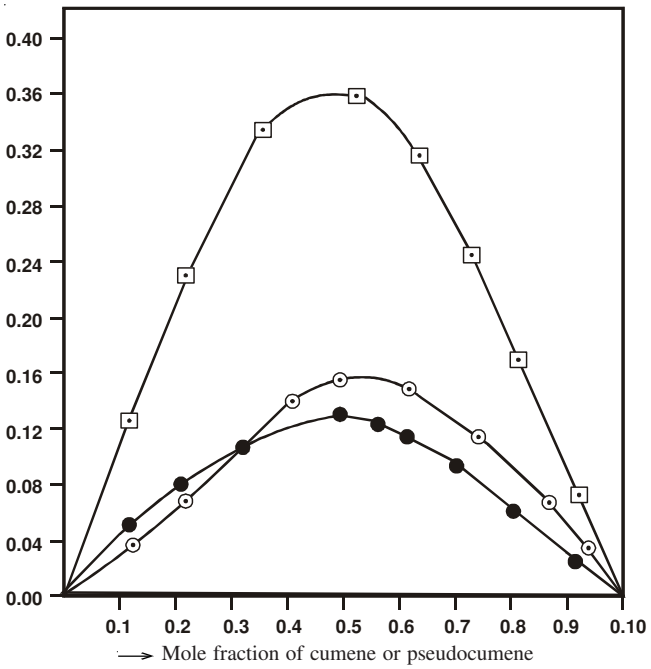

Fig. 1. Excess volume of mixing for (●): Pseudocumene + carbon tetrachloride. (⊙): Cumene + benzene. (⊡): Pseudocumene + benzene

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