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The Study Of Molecular Interaction And Excess Thermodynamic Properties Of Carbon Tetrachloride In Lower Alcohols

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ABSTRACT

The study of molecular interaction and excess thermodynamic properties in binary mixture of carbon tetrachloride and lower alcohols were reported at 298.15K. The molecular interaction have been carried out by computing various excess thermodynamic parameters i.e. density (ρ) viscosity (η) mole fraction (x) molar volumes (V) volume fraction (ϕ) excess gibbs free energy (ΔG^E) excess dynamic viscosity (η^E) excess molar volume (V^E) kinematic viscosity (λ), d_{12}, T_{12}, H_{12},η_{12}, Z_{12},Z_{21},(a)(b) & (c) and other constant The excess value of for said parameters have been evaluated by using data from density & viscosity of carbon tetra chloride in lower alcohols at 298.5K. The results of these parameters will conclude the nature and strength of molecular interaction.

Key words: -Mc Allister and Heric Brewer Parameters coefficients, Standard deviations.

Introduction: -

Thermodynamic properties of liquid mixtures play very important roles in understanding the physicochemical behavior and nature of intermolecular interaction. [1-3]

Deviation from ideal behavior of solutions can be expressed in terms of excess thermodynamic properties. Which give quantitative idea about the nature of molecular interactions. These may be known as difference between the Thermodynamic property of mixing for an actual liquid mixture. and the corresponding value for an ideal system at same temperatures, pressure and composition is called excess thermodynamic properties. [4-5]

Several research workers have calculated physical properties apart from various acoustic and thermodynamic parameters in pure solvents [6-7]

Present work deals with the study of the excess Gibbs free energy (ΔG^E), excess dynamic viscosity (η^E), excess molar volume (V^E), value of coefficient A, and standard deviation of these thermodynamic properties of carbon tetrachloride in lower alcohols at 298.15K In these system further report the value of interaction parameters d_{12}, T_{12}, H_{12}, η_{12}. [8-11] Mc Allister parameters (Z_{12} and Z_{21}).[12] Heric Brewer

parameters ('a' 'b' & 'c') [13] are being presented.

These values computed from the experimental values of excess Gibbs free energy (ΔG^E), excess dynamic viscosity (η^E), excess molar volume (V^E), excess molar volume (V), volume fraction (ϕ) mole fraction (x) by using density (ρ) viscosity (η) [14] obtained in the binary sytem .

Experimental: -

The density and viscosity were determined using a vibration densitometer DMA 48 filled model with a Hook G thermostat and Ubbelhode viscometer. The chemicals used in the study have been used pure and A-A. R: standard. The observation were reported with accuracy of $\pm$0.00002Kgm^{-3}and $\pm$0.0002 mpa.s respectively.

Computation of Physical parameters

Density (ρ):

$$\rho = \frac{m}{V+\pi r^2(h_1+h_2)}$$

'm': is the weight of the liquid

'r': is the radius of capillary

'h_1' & 'h_2': is the height of the liquid on capillaries

'v' : volume

Viscosity (η) :

$$\eta = \rho\ (at - \frac{b}{t})$$

'η': viscosity of liquid

'ρ': Density of liquid

't': time flow of liquid

'a' & 'b': Viscometric constant

Molar volume(V):

$$V = \frac{\vec{M}}{\rho}$$

'$\underset{M}{\rightarrow}$'= ($m_1 x_1 + m_2 x_2$)

x_1 and x_2 = mole fractions of component (1) and (2).

m_1 and m_2 = molar mass component (1) and (2).

'ρ': Density of binary system

Volume fraction (ϕ)

$$(\phi) = \frac{\text{The volume of liquid component}}{\text{Total volume of liquid mixture}}$$

Mole Fraction (x_1)

$$X_1 = \frac{\text{molarity of component (1)}}{\text{malarity of componet (1)+malarity of componet (2)}}$$

$X_2 = 1\text{-}X_1$

Excess molar volume (V^E) [15]

$(V^E) = V-(X_1 V_1 – X_2 V_2)$

V= molar volume of binary liquid system

V_1 and V_2 = molar volume of ideal component.

Excess dynamic viscosity (η^E) [16]

$(\eta^E) = \eta-(x_1 \eta_1 – x_2 \eta_2)$

η= observed viscosity of binary mixture

η_1 and η_2 = viscosities of component (1) and (2).

x_1 and x_2 = mole fractions of component (1) and (2).

Gibbs Free Energy (ΔG^E) [17]

$(\Delta G^E) = RT (\ln\eta v – x_1 \ln\eta_1 v_1 – x_2 \ln\eta_2 v_2)$

x_1 and x_2 = mole fraction of component (1) and (2).

η_1 and η_2 = viscosities of component (1) and (2).

v = observed viscosity of binary mixture

EXCESS PROPERTIES OF BINARY LIQUID MIXTURES AT 298.15K

TABLE 1: CCl_4 + Methanol

S. No.	(ϕ)	x_1	ρ ($g.cm^{-3}$)	η (m Pa.s)	η^E (m Pa.s)	V ($cm^3.mol^{-1}$)	V^E ($cm^3.mol^{-1}$)	ΔG^E ($J.mol^{-1}$)
1	0.00	0.0000	0.7868	0.547	0.000	40.725	0.000	00.00
2	0.10	0.0445	0.8726	0.576	0.011	43.155	-0.080	114.03
3	0.20	0.0949	0.9582	0.604	0.020	45.933	-0.141	213.80
4	0.30	0.1524	1.0420	0.633	0.027	10.120	-0.193	295.85
5	0.40	0.2185	1.1245	0.663	0.031	52.803	-0.239	358.99
6	0.50	0.2955	1.2058	0.697	0.034	57.105	-0.274	407.19
7	0.60	0.3862	1.2866	0.735	0.037	62.198	-0.292	433.49
8	0.70	0.4947	1.3664	0.779	0.039	68.296	-0.305	431.88
9	0.80	0.6266	1.4420	0.827	0.035	75.776	-0.259	376.08
10	0.90	0.7906	1.5152	0.878	0.022	85.118	-0.160	241.30
11	1.00	1.0000	1.5845	0.938	0.000	97.078	0.000	00.00

TABLE 2: CCl_4 + Ethanol System

S. No.	(ϕ)	x_1	ρ ($g.cm^{-3}$)	η (m Pa.s)	η^E (m Pa.s)	V ($cm^3.mol^{-1}$)	V^E ($cm^3.mol^{-1}$)	ΔG^E ($J.mol^{-1}$)
1	0.00	0.0000	0.7853	1.084	0.000	58.664	0.000	00.00
2	0.10	0.0629	0.8661	1.080	0.007	61.017	-0.064	37.44
3	0.20	0.1312	0.9469	1.078	0.013	63.585	-0.121	69.21
4	0.30	0.2057	1.0275	1.071	0.017	66.406	-0.160	93.33
5	0.40	0.2871	1.1080	1.060	0.018	69.406	-0.188	105.08
6	0.50	0.3767	1.1883	1.048	0.019	72.927	-0.206	119.92
7	0.60	0.4755	1.2684	1.035	0.020	76.711	-0.218	126.25
8	0.70	0.5851	1.3480	1.017	0.019	80.943	-0.196	119.80
9	0.80	0.7074	1.4272	0.995	0.014	85.683	-0.154	96.70
10	0.90	0.8447	1.5060	0.938	0.008	91.030	-0.089	59.16
11	1.00	1.0000	1.5845	0.938	0.000	97.780	0.000	00.00

TABLE 3: CCl_4 + 1-Propanol System

S. No.	(ϕ)	x_1	ρ ($g.cm^{-3}$)	η (m Pa.s)	η^E (m Pa.s)	V ($cm^3.mol^{-1}$)	V^E ($cm^3.mol^{-1}$)	ΔG^E ($J.mol^{-1}$)
1	0.00	0.0000	0.7997	1.898	0.000	75.145	0.000	00.00
2	0.10	0.0792	0.8788	1.827	0.005	76.827	-0.055	48.07
3	0.20	0.1621	0.9579	1.752	0.009	78.606	-0.095	92.62
4	0.30	0.2491	1.0367	1.671	0.012	80.490	-0.119	130.95
5	0.40	0.3404	1.1154	1.585	0.014	82.479	-0.132	163.16
6	0.50	0.4363	1.1941	1.494	0.015	84.575	-0.140	185.48
7	0.60	0.5373	1.2727	1.399	0.016	86.784	-0.145	197.29
8	0.70	0.6436	1.3510	1.295	0.015	89.132	-0.130	191.28
9	0.80	0.7559	1.4292	1.184	0.012	91.619	-0.105	162.40
10	0.90	0.8745	1.5070	1.066	0.007	94.261	-0.064	103.45
11	1.00	1.0000	1.5845	0.938	0.000	97.078	0.000	00.00

TABLE 4: Coefficients Ai and standard Deviation $\sigma(v^E)$ for Representation of Excess Molar Volume at 298.15 K.

System	A_0	A_1	A_2	$\sigma(V^E)$/ ($cm^3.mol^{-1}$)
CCl_4+				
Methanol	-1.1952	0.3021	0.0865	0.0086
Ethanol	-0.8539	0.1757	0.2292	0.0038
1-Propanol	-0.5761	0.0241	-0.0167	0.0035

TABLE 5: Coefficients Ai and standard Deviation $\sigma(\eta^E)$ for Representation of Excess Viscosities at 298.15 K.

System	A_0	A_1	A_2	$\sigma(\eta^E)$ / (mPa.s)
CCl_4+				
Methanol	0.1510	-0.0158	0.0374	0.0015
Ethanol	0.0801	-0.0101	0.0453	0.0000
1-Propanol	0.0633	0.0048	0.0036	0.0005

TABLE 6: Coefficients Ai and standard Deviation $\sigma(\Delta G^E)$ for Representation of Excess Gibbs Free Energy at 298.15 K.

System	A_0	A_1	A_2	$\sigma(\Delta G^E)/(J.mol^1)$
CCl_4/+				
Methanol	1715.3879	480.4559	242.4618	2.8412
Ethanol	504.3645	49.2847	96.9091	0.1196
1-Propanol	778.0677	180.5282	55.0941	0.6553

VALUES OF INTERACTION PARAMETERS AT 298.15K

TABLE 7: CCL_4 + Methanol System

S. No.	x_1	d_{12}	T_{12}	H_{12}	η_{12}
1	0.0000	E	E	E	E
2	0.0455	0.6284	0.8156	0.8727	1.3692
3	0.0949	0.5630	0.8121	0.8599	1.3251
4	0.1524	0.4979	0.8073	0.8461	1.2827
5	0.2185	0.4389	0.8025	0.8330	1.2454
6	0.2955	0.3983	0.8017	0.8253	1.2204
7	0.3862	0.3670	0.8035	0.8204	1.2014
8	0.4947	0.3463	0.8106	0.8200	1.1891
9	0.6266	0.3209	0.8159	0.8168	1.1740
10	0.7906	0.3835	0.8162	0.8090	1.1523
11	1.0000	E	E	E	E

TABLE 8: CCL_4 + Ethanol System

S. No.	x_1	d_{12}	T_{12}	H_{12}	η_{12}
1	0.0000	E	E	E	E
2	0.0629	0.1267	1.1130	1.0741	1.0654
3	0.1312	0.1182	1.1110	1.0691	1.0609
4	0.2057	0.1059	1.1069	1.0621	1.0544
5	0.2871	0.0923	1.1019	1.0543	1.0472
6	0.3767	0.0872	1.1007	1.0511	1.0446
7	0.4755	0.0890	1.1031	1.0515	1.0455
8	0.5851	0.0869	1.1034	1.0497	1.0444
9	0.7074	0.0796	1.1008	1.0452	1.0406
10	0.8447	0.0765	1.1003	1.0429	1.0390
11	1.0000	E	E	E	E

TABLE 9: CCL_4 + 1-Propanol System

S. No.	x_1	d_{12}	T_{12}	H_{12}	η_{12}
1	0.0000	E	E	E	E
2	0.0792	0.2405	1.5207	1.4507	1.1278
3	0.1621	0.2492	1.5219	1.4512	1.1327
4	0.2491	0.2562	1.5209	1.4494	1.1367
5	0.3404	0.2667	1.5217	1.4494	1.1426
6	0.4363	0.2779	1.5219	1.4489	1.1491
7	0.5373	0.2944	1.5245	1.4506	1.1586
8	0.6436	0.3109	1.5252	1.4505	1.1682
9	0.7559	0.3299	1.5254	1.4498	1.1793
10	0.8745	0.3556	1.5269	1.4503	1.1946
11	1.0000	E	E	E	E

TABLE 10: Value of McAliister Parameters ($Z_{12}$and Z_{21}) and Heric Brewer Parameters ('a', 'b' & 'c') at 298.15 K

S. No.	z_{121}	z_{21}	a/($cm^2.s^{-1}$)	b/($cm^2.s^{-1}$)	c/($cm^2.s^{-1}$)
CCl_4+					
Methanol	-0.1744	0.0012	-0.2935	0.2338	-0.1623
Ethanol	-0.9730	0.5528	-0.7404	0.4146	-0.2729
1-Propanol	0.3093	0.5530	-1.3208	0.6019	-0.2678

Variation of Excess molar volume V^E of binary liquid mixtures: CCl_4 with Methanol, Ethanol, Propanol as a function of mole fraction of CCl_4 (X_1) at 298.15K

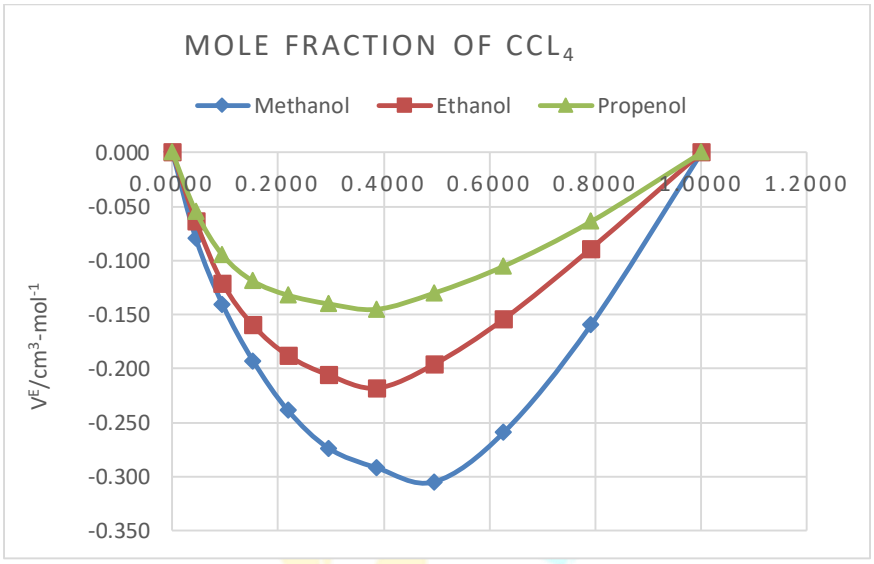

Fig. 01

Variation of Excess dynamic viscosity $\eta^E$of binary liquid mixtures: CCl_4 with Methanol, Ethanol, Propanol as a function of mole fraction of CCl_4 (X_1) at 298.15K

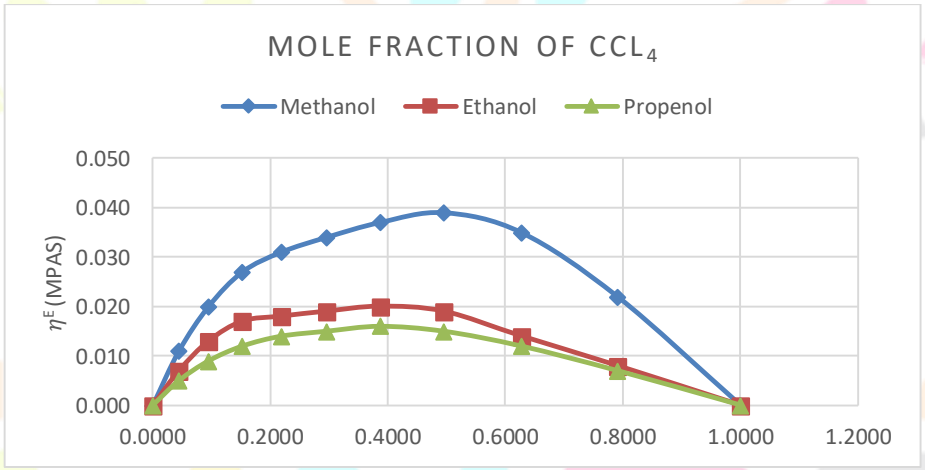

Fig. 02

Variation of Excess Gibbs Free energy (ΔG^E) of binary liquid mixtures: CCl_4 with Methanol, Ethanol, Propanol as a function of mole fraction of CCl_4 (X_1) at 298.15K

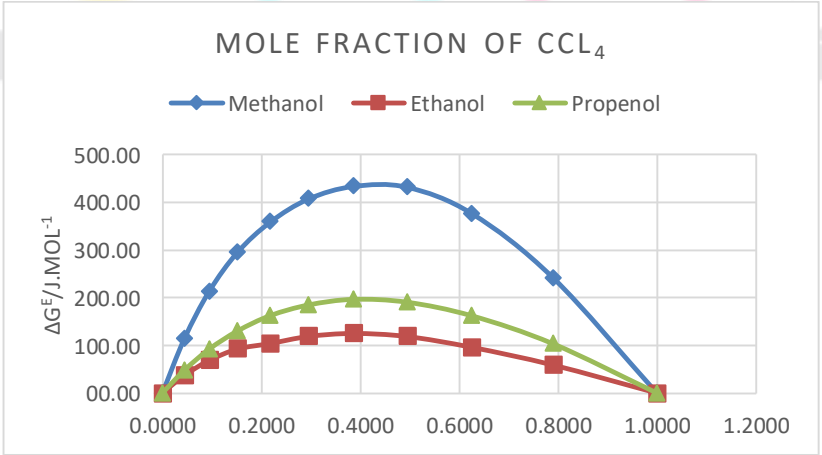

Fig. 03

Result &Discussion: -

Results abstained after determination Density & Viscosity of carbon tetra chloride in lower alcohols as binary system at 298.15K and the other acoustic and thermodynamic parameter η^E, V, V^E, ΔG^E and d_{12}, T_{12}, H_{12},η_{12}, computed were variable male fraction and volume fraction of carbon tetrachloride in lower alcohol binary mixture.

The result tabulated in table 1-10 the excess value of V^E, ΔG^E and $\eta^E$are plotted on the Fig No. 1, 2 and 3 at a variable mole fraction of carbon tetrachloride in lower alkanols at 298.15K, the comparative lines of graph of carbon tetra chloride in lower alkanols binary mixture conclude the nature and extent of molecular interaction of carbon tetra chloride with lower alkanals in binary mixture and interaction shown by line in fig 1,2 and 3.

The excess molar volume V^E have been evaluated from density values for all binary composition of CCl_4 + methanol, + Ethanal, +1 Propanol using apars equation related to excess molar volume the excremental data (table 1-3) reveals that all values of V^E are negatives which indicate strong specific interaction between the components and according to fig. 01. It is observed that far each binary mixture. The plot is parabola and minimum occur around 0.5 male fraction CCl_4 which confirm strong specific interaction.

The excess dynamic viscosity values have been evaluated using given above equation regarding this against mole faction range for binary liquid mixtures of CCl_4 + Methanol, + Ethanol, + 1-Prapasnal and are found to be positive as given in table 1,2,3 and according to fig-2 the plot of η^E vs CCl_4 male fraction is a parabolas shape all the binary mixtures.

The positive values of η^E with marked maxima indicate strong unlike interaction of molecule in solution. The ΔG^E value for binary liquid mixture of CCl_4+ lower alkanols have been evaluated using given equation with respect to mole fraction at 298.15K. All ΔG^E values are found to be positive which shows that the specific interaction is dominant in all the binary mixture in given table 1,2,3.

The plot ΔG^E vs (x_1) of CCl_4 with lower alkanals fig. 03 shows that maximum (0.5) complex formation or interaction at maxima of parabola.

The magnitude of ΔG^E should show the strength of chain length [18] of component.

Coefficient Ai and standard Deviation σX^E [19] have been evaluated with this equation using a computer ALPH 4000/ 300 S(VMS) system.

$$X^E = x_1 x_2[\sum_{i=0}^{K} Ai\ (x_1 - x_2)\ i]$$

where X^E V^E/cm^3or η^E/m pa.s and ΔG^E/ $J.mal^{-1}$

Standard deviation $\sigma(X^E)$ [20]

$$\sigma X^E = [\Sigma \frac{XE - XEcal}{\eta - p}]^{0.5}$$

Where n= No. of data points

P= No. of coefficient Ai

For all the binary mixtures of coefficients Ai and the standard deviation σX^E of $\sigma V^E, \sigma(\eta^E), \sigma(\Delta G^E)$ represent of their excess value in table no 4,5,6.

Viscosity model and molecular Interaction in binary system have been shown in table no 7,8,9 and logarithmic relation.[21] between the viscosity of the binary liquid mixture and its pure components.

$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12}$

d_{12} is a constant proportional to interchange energy (w). The variation of d_{12} with strength of interaction is almost similar to that of η^E.

The value of $d_{12}$are in general positive for systems in which strong interaction dominates and increases as the strength of interaction increases and order of CCl_4 with lower alcohols is Ethanol < Propanol < methanol viscosity of binary mixtures is represented by equation. [22]

$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2(x_1 x_2 \phi_1 \phi_2)^{.5} T_{12}$

Where T_{12} is interaction parameter which depend on temperature and composition of mixture ϕ_1 and ϕ_2 are the volume fraction x_1 x_2 are mole fractions and η_1 and η_2 are the viscosities of component (1) and (2).

The value of T_{12} given in table no 7, 8, 9 and order of interaction of CCl_4 in lower alcohol Methanol < ethanol < propanol.

The value of H_{12} evaluated by equation. [23]

$\eta = x_1^2 \eta_1 + x\eta_2 + 2x1x_2 H_{12}$

x_1, x_2 are mole fraction and η_1, η_2 are the viscosities of liquid component (1) and component (2) H_{12} measure of interaction strength between components and its knowns Hind interaction parameters. The value of H_{12} evaluated by above equation and are displayed in table no 7,8,9 for all binary mixtures the value of H_{12} are found to be positive indication strong interaction [24]and interaction order CCl_4 in lower alkanals.

The value of η_{12} is evaluated by equation.

$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12}$

η_{12} is known as Niadu interaction parameters and are shown in table no 7,8,9 η_{12} values are found to be positive for all the binary mixtures. The η_{12} is values hance interaction strength order of CCl_4 in lower alcohols is ethanol<1-propanol< methanol. The interaction parameters Z_{12} and Z_{21} have calculated by the relation [25]

$\ln \eta = x_1^3 \ln \eta_1 + 3x_1^2 x_2 \ln Z12 + 3x_1 x_2^2 \ln z_{21} + x_2^3 \ln \eta_2 - \ln (x_1 + x_2 M_1/ M_2) + 3x_1^2 x_2 \ln (2 + \frac{M2/M1}{3}) + 3x_1 x_2^2 \ln \eta_2 (1+2M_2/ M_1)/3 + X_2^3 \ln M_2/ M_1$

Viscosity (η) of binary liquid mixtures $x_1 x_2$ are mole fraction and η_1 η_2 are the viscosities m_1 and m_2 are molecular weight (1) and component (2).

The Mc Allister interaction parameters Z_{12} and Z_{21} are the measure of strength of interaction between the components, the value shown in table 10. z_{12}values are found tube negative for CCl_4 + lower alcohols. the Z_{12} value very in order of ethanol < methanol < 1-Propenol. However, Z_{21}value or positive and order in lower alcohols methanol < ethanol < 1-Propenol Heric and Brewer have proposed the relation.

$\lambda = x_1 \lambda_1 + x_2 \lambda_2 + x_2 x_2 (a + b (x_1 - x_2) + (x_1 - x_2)^2)$

Where $\lambda_1$and λ_2 are kinematic viscosities of components (1) and (2), a,b,c are the Heric-Brewer interaction parameter shown in table no -10

It is a observed that all the values of parameter a negative show the strong interaction between components in binary mixtures parameter (a) varies in the order by CCl4 mole fraction as methanol> ethanol> 1-propanol and interaction parameter (b) values are positive and order with CCl4 methanol< ethanol<1- propanol.

The value of parameter (c) value all thought all of them are negative

The present analysis suggests that McAllister and Heric Brewer model the data better than the viscosity models of parameters d_{12}, T_{12}, H_{12} and n_{12}.

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