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Notes

Estimation of cohesive force, energy of vaporization, heat of vaporization, cohesive energy density, solubility parameter and van der Waals constant of binary liquid mixtures using generalized hole theory

J D Pandey[a,*], Tanu Srivastava, Prakash Chandra, Rajput Prashant & D K Dwivedi[†]
Department of Chemistry, University of Allahabad, Allahabad 211002, India
Email: jdpandey@rediffmail.com

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Using the recently proposed generalized hole theory, the internal pressure, energy of vaporization, heat of vaporization, cohesive energy density, solubility parameter and van der Waals constant have been calculated for seven binary liquid mixtures, namely cyclohexane + cyclohexanol, *n*-heptane + toluene, *n*-heptane + *n*-hexane, cyclohexane + *n*-hexane, acetonitrile + benzene, benzene + dimethylformamide, and acetonitrile + dimethylformamide. Satisfactory results have been obtained for the studied systems.

Very recently, a generalized hole theory has been developed successfully from our lab and applied to pure liquids[1] and binary mixtures[2] for estimating the thermodynamic properties (isothermal compressibility, thermal expansivity and ultrasonic velocity). In all the cases the results were found to be very good when compared with the experimental values. This demonstrates the validity of the proposed hole theory. The basic idea of the theory is to assume the existence of holes in liquid. A liquid can be treated as a solution of molecules and holes. The appearance of holes can be regarded as a particular case of heterophase fluctuations. The holes can be treated as gas bubbles when these are large enough to accommodate a sufficient amount of vapours. Surface tension and internal pressure of pure liquid component are the only input data for estimating the hole radius, hole volume and hole creation energy in the present hole theory. From these three properties, it is possible to calculate all the thermodynamic as well as transport properties of liquids and liquid mixtures successfully. In the present note, an attempt has been made to extend the application of the proposed hole theory for assessing the magnitude of cohesive forces, estimating the cohesive energy density (CED), solubility parameter (δ), energy of vaporization (ΔE_v), heat of vaporization (ΔH_v), and van der Waals constant (a) in the case of binary liquid mixtures. The significance of the above mentioned parameters has been discussed earlier by several workers[3-6]. Flory theory has been earlier used to study the internal pressure[14,15] and van der Waals constant in the case of binary liquid mixtures.

Hildebrand, Scott and Scatchard while suggesting the improvement of van Laar`s Theory, defined a new parameter, called cohesive energy density given as:

$$C_i = \frac{\Delta U_i^{vap}}{V_i}$$

where ΔU_i^{vap} is the energy of complete vaporization, that is, the energy change accompanying the isothermal vaporization of the state liquid to the ideal gas state. Cohesive energy density reflects intermolecular forces between molecules of components. The CED is related to the internal pressure by, $\text{CED} = \frac{\Delta U_i^{vap}}{V_i} = P_{\text{int}}$. This equivalency has been discussed by a number of workers[8,10].

The generalized hole theory has been extended here to estimate the aforesaid parameters for the seven binary mixtures [cyclohexane (x_1) + cyclohexanol (x_2)(I), *n*-heptane (x_1)+ toluene (x_2)(II), *n*-heptane (x_1)+*n*-hexane (x_2)(III), cyclohexane (x_1) + *n*-hexane (x_2)(IV), acetonitrile (x_1) + benzene (x_2)(V), benzene (x_1)+ dimethylformamide (x_2)(VI) and acetonitrile (x_1) + dimethylformamide (x_2)(VII)] at 298.15 K. The calculated values of internal pressure and other properties of these mixtures are compared with earlier findings[11-14].

Theoretical

In the usual theory of density fluctuations in solid and liquid, such variation of density is only to be connected with a general increase or decrease of the

[†]Present address: Indian Institute of Legal Meteorology, Ranchi, India

intermolecular distances distorting the homogeneity of the body in small volumes. The appearance of hole in a liquid can be regarded as a particular case of heterophase fluctuations. Inside the liquid, there is a balance between attractive and repulsive forces that gives rise to what is called the internal pressure. The internal pressure of a binary liquid mixture, $(P_{int})_{12}$, is given by Eq. (1),

$$(P_{int})_{12} = \frac{\alpha_{12}T}{\beta_{T(12)}} - P \quad \ldots (1)$$

where α_{12} and $\beta_{T(12)}$ are respectively, the thermal expansivity and isothermal compressibility of binary liquid mixture having components 1 and 2. The expressions for α_{12} and $\beta_{T(12)}$ have been deduced in our recent paper[2] on the basis of the newly developed hole theory, and given by Eqs (2) and (3) respectively.

$$\alpha_{12} = \frac{1}{V_{12}kT^2} aNV_{h(12)} \left[\exp\left(1-\frac{1}{a}\right) \exp\left(\frac{E_{h(12)} + PV_{h(12)}}{kT}\right)\right] \times \frac{\left[E_{h(12)} + PV_{h(12)}\right]}{\left[\exp\left(1-\frac{1}{a}\right)\exp\left(\frac{E_{h(12)} + PV_{h(12)}}{kT}\right) - 1\right]^2} \quad \ldots (2)$$

$$\beta_{T(12)} = \frac{aNV_{h(12)}^2 \exp\left(1-\frac{1}{a}\right)\exp\left(\frac{E_{h(12)} + PV_{h(12)}}{kT}\right)}{V_{(12)}kT\left[\exp\left(1-\frac{1}{a}\right)\exp\left(\frac{E_{h(12)} + PV_{h(12)}}{kT}\right) - 1\right]^2} \quad \ldots (3)$$

Here all the symbols have their usual significance as mentioned earlier[2]. Internal pressure of binary liquid mixture, $(P_{int})_{12}$, has been calculated from the values of α_{12} and $\beta_{T(12)}$ obtained from Eqs (2) and (3) using Eq (1). A rough estimate of the energy of vaporization (ΔE_v), solubility parameter (δ), cohesive energy density (CED), heat of vaporization (ΔH_v) and van der Waals constant (a) are calculated from Eqs (4) to (8).

$$\Delta E_v = (P_{nt})_{12} V_m \quad \ldots (4)$$

$$\text{Solubility parameter, } \delta_{12} = \sqrt{(P_{int})_{12}} = \sqrt{\frac{\Delta E_v}{V_m}} \quad \ldots (5)$$

$$CED = \frac{\Delta E_v}{V_m} \quad \ldots (6)$$

$$\Delta E_v = \Delta H_v + RT \quad \ldots (7)$$

$$a = (P_{int})_{12} V_m^2 \quad \ldots (8)$$

Results and discussion

The thermodynamic parameters viz. internal pressure $(P_{int})_{12}$, energy of vaporization (ΔE_v), cohesive energy density (CED), solubility parameter (δ), heat of vaporization (ΔH_v) and van der Waals constant, a ,have been computed at 298.15K for the seven binary mixtures and compared with its experimental findings. The calculated values of α, β and P_{int} at 298.15K for pure liquids are recorded in Table 1. The above thermodynamic parameters are calculated from Eqs (4) to (8). The results are shown in Table 2. All the aforesaid thermodynamic properties have been reported along with the average percentage deviations.

For the binary systems (I), (II), (V), (VI) and (VII), the values of internal pressure decrease with the increase in mole fractions of the first components, while, for the binary systems (III) and (IV), the internal pressure varies directly with the mole fractions of the first components. It is worthwhile to mention that the agreement between the observed and calculated values of internal pressure is good for all the systems and excellent for the systems (IV) and (V).

As far as the energy of vaporization for the investigated binary mixtures is concerned, it is observed that the energy of vaporization increases with the mole fractions of the first components for the systems, (II), (III), (IV) and (VI), whereas energy of vaporization varies inversely with the mole fraction of the first components for the systems, (I), (V) and (VII). It is obvious from the values reported that the

Table 1 – Calculated values of isothermal compressibility, thermal expansivity and internal pressure of pure liquids at 298.15K

Liquids	β_T $(m^2/N)x10^{11}$	α_T $(K^{-1})x10^3$	P_i $(N/m^2)x10^8$
Cyclohexane	112.70	1.16	3.068802
Cyclohexanol	59.07	.804	4.058111
Toluene	90.20	1.23	4.065682
n-Hexane	172.20	1.13	1.956501
n-Heptane	142.40	1.08	2.26125
Benzene	97.30	1.23	3.769008
Dimethylformamide	54.780	.5590	3.042458
Acetonitrile	111.67	1.3720	3.663131

Table 2 – Calculated and experimental values of P_{int}, ΔE_{vap}, CED, δ, ΔH_v and a at 298.15K for the binary mixtures

x_1	P_{int} ($Nm^{-2}x10^8$) Expt. (Calc.)	Δ (%)	ρ_{mix} (g cm^{-3})	V_m (cm^3 mol^{-1})	ΔE_v ($Jmol^{-1}$) Expt. (Calc.)	CED (J cm^{-3}) Expt. (Calc.)	δ ($J^{1/2}cm^{-3/2}$) Expt. (Calc.)	Δ (%)	ΔH_v ($Jmol^{-1}$) Expt. (Calc.)	Δ %	a (atm l^2)
					Cyclohexane(x_1)+Cyclohexanol(x_2)						
	4.03				4.29E+04	1.68E+03	4.10E+01		45368		45.05
0.0999	(3.94)	2.23	0.93	106.42	(4.19E+04)	(1.65E+03)	(4.06E+01)	1.12	(4.44E+04)	2.11	(44.04)
	3.95				4.22E+04	1.65E+03	4.06E+01		4.47E+04		44.59
0.2129	(3.82)	3.29	0.91	106.95	(4.09E+04)	(1.60E+03)	(4.00E+01)	1.66	(4.33E+04)	3.11	(43.13)
	3.89				4.18E+04	1.63E+03	4.03E+01		4.43E+04		44.33
0.3172	(3.72)	4.37	0.89	107.45	(4.00E+04)	(1.55E+03)	(3.94E+01)	2.21	(4.25E+04)	4.13	(42.39)
	3.64				3.94E+04	1.52E+03	3.90E+01		4.19E+04		42.19
0.4950	(3.57)	1.92	0.86	108.36	(3.87E+04)	(1.49E+03)	(3.86E+01)	0.97	(4.12E+04)	1.81	(41.38)
	3.55				3.86E+04	1.48E+03	3.85E+01		4.11E+04		41.50
0.5815	(3.50)	1.41	0.85	108.83	(3.81E+04)	(1.46E+03)	(3.82E+01)	0.71	(4.06E+04)	1.32	(40.91)
	3.45				3.77E+04	1.44E+03	3.80E+01		4.02E+04		40.75
0.6822	(3.43)	0.58	0.83	109.39	(3.75E+04)	(1.43E+03)	(3.79E+01)	0.29	(4.00E+04)	0.54	(40.51)
	3.27				3.60E+04	1.37E+03	3.70E+01		3.85E+04		39.12
0.8023	(3.35)	-2.45	0.81	110.10	(3.69E+04)	(1.40E+03)	(3.74E+01)	-1.22	(3.94E+04)	-2.29	(40.08)
	APD	2.32					APD	1.17	APD	2.19	
					n-Heptane(x_1)+Toluene(x_2)						
	3.08				3.61E+04	1.29E+03	3.59E+01		3.85E+04		41.65
0.2979	(3.31)	-7.47	0.81	117.05	(3.87E+04)	(1.38E+03)	(3.72E+01)	-3.67	(4.12E+04)	-6.99	(44.76)
	3.06				3.60E+04	1.28E+03	3.58E+01		3.85E+04		41.85
0.3162	(3.30)	-7.84	0.80	117.72	(3.88E+04)	(1.38E+03)	(3.71E+01)	-3.85	(4.13E+04)	-7.34	(45.14)
	3.04				3.60E+04	1.27E+03	3.56E+01		3.84E+04		42.01
0.3325	(3.29)	-8.22	0.80	118.32	(3.89E+04)	(1.38E+03)	(3.71E+01)	-4.03	(4.14E+04)	-7.69	(45.46)
	3.02				3.60E+04	1.26E+03	3.55E+01		3.84E+04		42.24
0.3519	(3.27)	-8.28	0.80	119.04	(3.89E+04)	(1.37E+03)	(3.70E+01)	-4.06	(4.14E+04)	-7.74	(45.74)
	3.01				3.60E+04	1.26E+03	3.55E+01		3.85E+04		42.60
0.3707	(3.26)	-8.31	0.79	119.75	(3.90E+04)	(1.36E+03)	(3.69E+01)	-4.07	(4.15E+04)	-7.77	(46.14)
	2.99				3.60E+04	1.25E+03	3.54E+01		3.85E+04		42.84
0.3902	(3.25)	-8.70	0.79	120.49	(3.92E+04)	(1.36E+03)	(3.69E+01)	-4.26	(4.16E+04)	-8.14	(46.57)
	2.98				3.60E+04	1.25E+03	3.53E+01		3.85E+04		43.04
0.4029	(3.24)	-8.72	0.79	120.97	(3.92E+04)	(1.35E+03)	(3.68E+01)	-4.27	(4.17E+04)	-8.16	(46.80)
	2.96				3.61E+04	1.24E+03	3.52E+01		3.86E+04		43.44
0.4282	(3.22)	-8.78	0.78	121.94	(3.93E+04)	(1.35E+03)	(3.67E+01)	-4.30	(4.17E+04)	-8.22	(47.26)
	2.94				3.61E+04	1.23E+03	3.51E+01		3.86E+04		43.71
0.4484	(3.21)	-9.18	0.78	122.73	(3.94E+04)	(1.34E+03)	(3.66E+01)	-4.49	(4.19E+04)	-8.59	(47.72)
	2.93				3.62E+04	1.22E+03	3.50E+01		3.87E+04		44.12
0.4684	(3.19)	-8.87	0.78	123.51	(3.94E+04)	(1.33E+03)	(3.65E+01)	-4.34	(4.19E+04)	-8.30	(48.03)
	2.91				3.62E+04	1.22E+03	3.49E+01		3.86E+04		44.35
0.4874	(3.18)	-9.28	0.77	124.27	(3.95E+04)	(1.33E+03)	(3.65E+01)	-4.54	(4.20E+04)	-8.68	(48.47)
	2.9				3.62E+04	1.21E+03	3.48E+01		3.87E+04		44.62
0.5023	(3.16)	-8.97	0.77	124.86	(3.95E+04)	(1.32E+03)	(3.63E+01)	-4.39	(4.19E+04)	-8.39	(48.63)
	2.89				3.63E+04	1.21E+03	3.48E+01		3.88E+04		45.06
0.5227	(3.15)	-9.00	0.77	125.68	(3.96E+04)	(1.32E+03)	(3.63E+01)	-4.40	(4.21E+04)	-8.42	(49.11)
	2.87				3.63E+04	1.20E+03	3.46E+01		3.88E+04		45.37
0.5442	(3.13)	-9.06	0.76	126.56	(3.96E+04)	(1.31E+03)	(3.62E+01)	-4.43	(4.21E+04)	-8.48	(49.48)
	2.86				3.64E+04	1.20E+03	3.46E+01		3.89E+04		45.81
0.5646	(3.11)	-8.74	0.76	127.40	(3.96E+04)	(1.30E+03)	(3.61E+01)	-4.28	(4.21E+04)	-8.18	(49.82)
	APD	8.63					APD	4.23	APD	8.07	
					n-Heptane(x_1)+n-Hexane(x_2)						
	2.67				3.72E+04	1.12E+03	3.34E+01		3.96E+04		51.06
0.4704	(2.66)	0.37	0.67	139.19	(3.70E+04)	(1.11E+03)	(3.33E+01)	0.19	(3.95E+04)	0.35	(50.87)
	2.69				3.73E+04	1.12E+03	3.35E+01		3.97E+04		50.96
0.4299	(2.65)	1.49	0.67	138.55	(3.67E+04)	(1.11E+03)	(3.33E+01)	0.75	(3.92E+04)	1.39	(50.21)
	2.7				3.75E+04	1.13E+03	3.36E+01		4.00E+04		51.37
0.4486	(2.65)	1.85	0.67	138.84	(3.68E+04)	(1.11E+03)	(3.33E+01)	0.93	(3.93E+04)	1.74	(50.42)
	2.71				3.77E+04	1.13E+03	3.37E+01		4.02E+04		51.82
0.4704	(2.66)	1.85	0.67	139.19	(3.70E+04)	(1.11E+03)	(3.33E+01)	0.93	(3.95E+04)	1.73	(50.87)
	2.73				3.81E+04	1.14E+03	3.38E+01		4.06E+04		52.46
0.4919	(2.66)	2.56	0.67	139.54	(3.71E+04)	(1.11E+03)	(3.33E+01)	1.29	(3.96E+04)	2.41	(51.12)
	2.75				3.85E+04	1.15E+03	3.39E+01		4.09E+04		53.08
0.5114	(2.67)	2.91	0.67	139.85	(3.73E+04)	(1.12E+03)	(3.34E+01)	1.47	(3.98E+04)	2.73	(51.54)

Contd

Table 2 – Calculated and experimental values of P_{int}, ΔE_{vap}, CED, δ, ΔH_v and a at 298.15K for the binary mixtures—*Contd*

x_1	P_{int} ($Nm^{-2}x10^8$) Expt. (Calc.)	Δ (%)	ρ_{mix} (g cm^{-3})	V_m (cm^3 mol^{-1})	ΔE_v ($Jmol^{-1}$) Expt. (Calc.)	CED (J cm^{-3}) Expt. (Calc.)	δ ($J^{1/2}cm^{-3/2}$) Expt. (Calc.)	Δ (%)	ΔH_v ($Jmol^{-1}$) Expt. (Calc.)	Δ %	a (atm l^2)
					n-Heptane(x_1)+n-Hexane(x_2) Contd						
	2.77				3.88E+04	1.16E+03	3.40E+01		4.13E+04		53.68
0.5290	(2.67)	3.61	0.67	140.12	(3.74E+04)	(1.12E+03)	(3.34E+01)	1.82	(3.99E+04)	3.39	(51.74)
	2.78				3.90E+04	1.16E+03	3.41E+01		4.15E+04		54.12
0.5491	(2.67)	3.96	0.67	140.44	(3.75E+04)	(1.12E+03)	(3.34E+01)	2.00	(4.00E+04)	3.72	(51.98)
	2.79				3.92E+04	1.17E+03	3.41E+01		4.17E+04		54.43
0.5584	(2.68)	3.94	0.67	140.59	(3.77E+04)	(1.12E+03)	(3.35E+01)	1.99	(4.02E+04)	3.71	(52.28)
	2.82				3.98E+04	1.18E+03	3.43E+01		4.23E+04		55.38
0.5880	(2.68)	4.96	0.67	141.06	(3.78E+04)	(1.12E+03)	(3.35E+01)	2.51	(4.03E+04)	4.67	(52.63)
	2.85				4.03E+04	1.19E+03	3.45E+01		4.28E+04		56.23
0.6088	(2.69)	5.61	0.67	141.39	(3.80E+04)	(1.12E+03)	(3.35E+01)	2.85	(4.05E+04)	5.29	(53.08)
	2.87				4.07E+04	1.20E+03	3.46E+01		4.31E+04		56.86
0.6275	(2.69)	6.27	0.67	141.68	(3.81E+04)	(1.12E+03)	(3.35E+01)	3.19	(4.06E+04)	5.91	(53.30)
	2.89				4.10E+04	1.21E+03	3.48E+01		4.35E+04		57.49
0.6453	(2.70)	6.57	0.67	141.96	(3.83E+04)	(1.13E+03)	(3.36E+01)	3.34	(4.08E+04)	6.20	(53.71)
	2.91				4.14E+04	1.22E+03	3.49E+01		4.39E+04		58.12
0.6637	(2.70)	7.22	0.67	142.25	(3.84E+04)	(1.13E+03)	(3.36E+01)	3.68	(4.09E+04)	6.81	(53.93)
	2.93				4.18E+04	1.22E+03	3.50E+01		4.42E+04		58.77
0.6829	(2.70)	7.85	0.67	142.55	(3.85E+04)	(1.13E+03)	(3.36E+01)	4.01	(4.10E+04)	7.41	(54.16)
	APD	4.07					APD	2.06	APD	3.83	
					Cyclohexane(x_1)+n-Hexane(x_2)						
	2.71				3.43E+04	1.13E+03	3.37E+01		3.67E+04		42.77
0.2227	(2.75)	-1.48	0.68	126.45	(3.48E+04)	(1.15E+03)	(3.39E+01)	-0.74	(3.73E+04)	-1.38	(43.40)
	2.73				3.42E+04	1.14E+03	3.38E+01		3.67E+04		42.40
0.2689	(2.77)	-1.47	0.69	125.44	(3.47E+04)	(1.16E+03)	(3.40E+01)	-0.73	(3.72E+04)	-1.37	(43.02)
	2.75				3.42E+04	1.15E+03	3.39E+01		3.67E+04		42.02
0.3158	(2.80)	-1.82	0.69	124.43	(3.48E+04)	(1.17E+03)	(3.42E+01)	-0.90	(3.73E+04)	-1.70	(42.79)
	2.77				3.42E+04	1.16E+03	3.40E+01		3.67E+04		41.71
0.3588	(2.82)	-1.81	0.70	123.51	(3.48E+04)	(1.18E+03)	(3.43E+01)	-0.90	(3.73E+04)	-1.68	(42.46)
	2.79				3.42E+04	1.17E+03	3.41E+01		3.67E+04		41.40
0.4016	(2.85)	-2.15	0.70	122.62	(3.49E+04)	(1.19E+03)	(3.45E+01)	-1.07	(3.74E+04)	-2.01	(42.29)
	2.81				3.42E+04	1.17E+03	3.43E+01		3.67E+04		41.12
0.4433	(2.87)	-2.14	0.71	121.76	(3.49E+04)	(1.20E+03)	(3.46E+01)	-1.06	(3.74E+04)	-1.99	(42.00)
	2.83				3.42E+04	1.18E+03	3.44E+01		3.67E+04		40.82
0.4861	(2.89)	-2.12	0.71	120.89	(3.49E+04)	(1.21E+03)	(3.48E+01)	-1.05	(3.74E+04)	-1.98	(41.69)
	2.85				3.42E+04	1.19E+03	3.45E+01		3.67E+04		40.55
0.527	(2.92)	-2.46	0.72	120.07	(3.51E+04)	(1.22E+03)	(3.49E+01)	-1.22	(3.75E+04)	-2.29	(41.55)
	2.87				3.42E+04	1.20E+03	3.46E+01		3.67E+04		40.34
0.5642	(2.94)	-2.44	0.72	119.33	(3.51E+04)	(1.23E+03)	(3.51E+01)	-1.21	(3.76E+04)	-2.27	(41.32)
	2.89				3.43E+04	1.21E+03	3.48E+01		3.68E+04		40.12
0.6019	(2.96)	-2.42	0.73	118.60	(3.51E+04)	(1.24E+03)	(3.52E+01)	-1.20	(3.76E+04)	-2.26	(41.09)
	2.91				3.43E+04	1.22E+03	3.49E+01		3.68E+04		39.88
0.6414	(2.98)	-2.41	0.73	117.83	(3.51E+04)	(1.25E+03)	(3.53E+01)	-1.20	(3.76E+04)	-2.24	(40.84)
	2.93				3.49E+04	1.22E+03	3.50E+01		3.74E+04		40.97
0.5795	(3.01)	-2.73	0.72	119.03	(3.58E+04)	(1.26E+03)	(3.55E+01)	-1.36	(3.83E+04)	-2.55	(42.09)
	2.96				3.45E+04	1.24E+03	3.52E+01		3.69E+04		39.59
0.7164	(3.03)	-2.36	0.74	116.41	(3.53E+04)	(1.27E+03)	(3.56E+01)	-1.18	(3.78E+04)	-2.21	(40.53)
	2.98				3.45E+04	1.25E+03	3.53E+01		3.70E+04		39.41
0.7521	(3.05)	-2.35	0.74	115.75	(3.53E+04)	(1.27E+03)	(3.57E+01)	-1.17	(3.78E+04)	-2.19	(40.33)
	3.01				3.46E+04	1.26E+03	3.55E+01		3.71E+04		39.35
0.7877	(3.07)	-1.99	0.75	115.09	(3.53E+04)	(1.28E+03)	(3.58E+01)	-0.99	(3.78E+04)	-1.86	(40.14)
	APD	2.14					APD	1.07	APD	2.00	
					Acetonitrile(x_1)+Benzene(x_2)						
	3.73				3.30E+04	1.56E+03	3.95E+01		3.54E+04		28.74
0.0325	(3.76)	-0.80	0.87	88.35	(3.32E+04)	(1.57E+03)	(3.96E+01)	-0.40	(3.57E+04)	-0.75	(28.97)
	3.73				3.28E+04	1.56E+03	3.95E+01		3.53E+04		28.54
0.0416	(3.76)	-0.80	0.87	88.05	(3.31E+04)	(1.57E+03)	(3.96E+01)	-0.40	(3.56E+04)	-0.75	(28.77)
	3.74				3.17E+04	1.56E+03	3.95E+01		3.42E+04		26.49
0.142	(3.75)	-0.27	0.86	84.72	(3.18E+04)	(1.57E+03)	(3.96E+01)	-0.13	(3.42E+04)	-0.25	(26.56)
	3.74				3.02E+04	1.56E+03	3.95E+01		3.27E+04		24.09
0.2578	(3.74)	0.00	0.85	80.78	(3.02E+04)	(1.56E+03)	(3.95E+01)	0.00	(3.27E+04)	0.00	(24.09)

Contd

Table 2 – Calculated and experimental values of P_{int}, ΔE_{vap}, CED, δ, ΔH_v and a at 298.15K for the binary mixtures—*Contd*

x_1	P_{int} ($Nm^{-2}x10^8$) Expt. (Calc.)	Δ (%)	ρ_{mix} (g cm^{-3})	V_m (cm^3 mol^{-1})	ΔE_v ($Jmol^{-1}$) Expt. (Calc.)	CED (J cm^{-3}) Expt. (Calc.)	δ ($J^{1/2}cm^{-3/2}$) Expt. (Calc.)	Δ (%)	ΔH_v ($Jmol^{-1}$) Expt. (Calc.)	Δ %	a (atm l^2)
					Acetonitrile(x_1)+Benzene(x_2) Contd						
	3.73				2.88E+04	1.56E+03	3.95E+01		3.13E+04		21.98
0.3588	(3.74)	-0.27	0.84	77.26	(2.89E+04)	(1.56E+03)	(3.95E+01)	-0.13	(3.14E+04)	-0.25	(22.04)
	3.71				2.71E+04	1.55E+03	3.94E+01		2.96E+04		19.57
0.4751	(3.73)	-0.54	0.83	73.11	(2.73E+04)	(1.56E+03)	(3.95E+01)	-0.27	(2.97E+04)	-0.49	(19.68)
	3.68				2.55E+04	1.54E+03	3.92E+01		2.80E+04		17.45
0.5786	(3.72)	-1.09	0.82	69.31	(2.58E+04)	(1.55E+03)	(3.94E+01)	-0.54	(2.83E+04)	-0.99	(17.64)
	3.66				2.38E+04	1.53E+03	3.91E+01		2.63E+04		15.31
0.6908	(3.70)	-1.09	0.81	65.09	(2.41E+04)	(1.55E+03)	(3.93E+01)	-0.54	(2.66E+04)	-0.99	(15.47)
	3.63				2.22E+04	1.52E+03	3.90E+01		2.47E+04		13.44
0.7902	(3.69)	-1.65	0.80	61.26	(2.26E+04)	(1.54E+03)	(3.93E+01)	-0.82	(2.51E+04)	-1.49	(13.67)
	3.62				2.07E+04	1.51E+03	3.89E+01		2.31E+04		11.63
0.8962	(3.68)	-1.66	0.79	57.06	(2.10E+04)	(1.54E+03)	(3.92E+01)	-0.83	(2.35E+04)	-1.48	(11.83)
	3.61				1.95E+04	1.51E+03	3.88E+01		2.19E+04		10.35
0.9743	(3.67)	-1.66	0.78	53.90	(1.98E+04)	(1.53E+03)	(3.92E+01)	-0.83	(2.23E+04)	-1.47	(10.52)
	APD	0.89					APD	0.44	APD	0.81	
					Benzene (x_1)+Dimethylformamide(x_2)						
	3.07				2.73E+04	1.28E+03	3.58E+01		2.98E+04		24.04
0.0258	(3.05)	0.65	0.88	89.07	(2.72E+04)	(1.27E+03)	(3.57E+01)	0.33	(2.96E+04)	0.60	(23.89)
	3.26				2.87E+04	1.36E+03	3.69E+01		3.12E+04		24.97
0.1031	(3.08)	5.52	0.88	88.09	(2.71E+04)	(1.29E+03)	(3.59E+01)	2.80	(2.96E+04)	5.08	(23.59)
	3.42				2.97E+04	1.43E+03	3.78E+01		3.21E+04		25.40
0.2089	(3.43)	-0.29	0.89	86.75	(2.98E+04)	(1.43E+03)	(3.79E+01)	-0.15	(3.22E+04)	-0.27	(25.48)
	3.61				3.09E+04	1.51E+03	3.88E+01		3.33E+04		26.02
0.3129	(3.80)	-5.26	0.90	85.46	(3.25E+04)	(1.59E+03)	(3.99E+01)	-2.60	(3.50E+04)	-4.87	(27.39)
	3.72				3.13E+04	1.55E+03	3.94E+01		3.38E+04		26.00
0.4203	(3.87)	-4.03	0.90	84.15	(3.26E+04)	(1.62E+03)	(4.02E+01)	-2.00	(3.50E+04)	-3.74	(27.05)
	3.79				3.15E+04	1.58E+03	3.98E+01		3.39E+04		25.77
0.5167	(3.94)	-3.96	0.91	82.99	(3.27E+04)	(1.65E+03)	(4.06E+01)	-1.96	(3.52E+04)	-3.67	(26.79)
	3.82				3.12E+04	1.60E+03	4.00E+01		3.37E+04		25.18
0.6247	(4.03)	-5.50	0.92	81.72	(3.29E+04)	(1.68E+03)	(4.10E+01)	-2.71	(3.54E+04)	-5.09	(26.56)
	3.83				3.09E+04	1.60E+03	4.00E+01		3.34E+04		24.59
0.7168	(4.12)	-7.57	0.92	80.65	(3.32E+04)	(1.72E+03)	(4.15E+01)	-3.72	(3.57E+04)	-7.01	(26.45)
	3.81				3.02E+04	1.59E+03	3.99E+01		3.27E+04		23.70
0.8262	(3.54)	7.09	0.93	79.39	(2.81E+04)	(1.48E+03)	(3.85E+01)	3.61	(3.06E+04)	6.55	(22.02)
	3.76				2.94E+04	1.57E+03	3.96E+01		3.19E+04		22.66
0.9373	(3.67)	2.39	0.94	78.14	(2.87E+04)	(1.53E+03)	(3.92E+01)	1.20	(3.12E+04)	2.21	(22.12)
	3.73				2.90E+04	1.56E+03	3.95E+01		3.15E+04		22.23
0.9762	(3.73)	0.00	0.94	77.71	(2.90E+04)	(1.56E+03)	(3.95E+01)	0.00	(3.15E+04)	0.00	(22.23)
	APD	3.84					APD	1.92	APD	3.55	
					Acetonitrile (x_1)+Dimethylformamide(x_2)						
	3.02				2.70E+04	1.26E+03	3.55E+01		2.95E+04		23.81
0.0011	(3.04)	-0.66	0.87	89.37	(2.72E+04)	(1.27E+03)	(3.56E+01)	-0.33	(2.96E+04)	-0.61	(23.97)
	3.15				2.71E+04	1.32E+03	3.63E+01		2.96E+04		23.01
0.1030	(3.06)	2.86	0.86	86.02	(2.63E+04)	(1.28E+03)	(3.58E+01)	1.44	(2.88E+04)	2.62	(22.35)
	3.28				2.71E+04	1.37E+03	3.70E+01		2.96E+04		22.09
0.2045	(3.09)	5.79	0.85	82.61	(2.55E+04)	(1.29E+03)	(3.59E+01)	2.94	(2.80E+04)	5.31	(20.81)
	3.32				2.62E+04	1.39E+03	3.73E+01		2.87E+04		20.38
0.3132	(3.12)	6.02	0.84	78.86	(2.46E+04)	(1.30E+03)	(3.61E+01)	3.06	(2.71E+04)	5.50	(19.15)
	3.33				2.55E+04	1.39E+03	3.73E+01		2.80E+04		19.24
0.3798	(3.14)	5.71	0.84	76.52	(2.40E+04)	(1.31E+03)	(3.62E+01)	2.89	(2.65E+04)	5.20	(18.15)
	3.36				2.39E+04	1.40E+03	3.75E+01		2.63E+04		16.74
0.5318	(3.20)	4.76	0.82	71.04	(2.27E+04)	(1.34E+03)	(3.66E+01)	2.41	(2.52E+04)	4.31	(15.94)
	3.38				2.28E+04	1.41E+03	3.76E+01		2.53E+04		15.24
0.6248	(3.25)	3.85	0.81	67.59	(2.20E+04)	(1.36E+03)	(3.69E+01)	1.94	(2.44E+04)	3.47	(14.65)
	3.65				2.30E+04	1.53E+03	3.91E+01		2.55E+04		14.34
0.7431	(3.33)	8.77	0.80	63.08	(2.10E+04)	(1.39E+03)	(3.73E+01)	4.48	(2.35E+04)	7.92	(13.08)
	3.66				2.16E+04	1.53E+03	3.91E+01		2.41E+04		12.61
0.8453	(3.43)	6.28	0.79	59.09	(2.03E+04)	(1.43E+03)	(3.79E+01)	3.19	(2.27E+04)	5.64	(11.82)
	3.63				1.99E+04	1.52E+03	3.90E+01		2.24E+04		10.82
0.9486	(3.57)	1.65	0.78	54.95	(1.96E+04)	(1.49E+03)	(3.86E+01)	0.83	(2.21E+04)	1.47	(10.64)
	3.62				1.95E+04	1.51E+03	3.89E+01		2.20E+04		10.41
0.9724	(3.61)	0.28	0.78	53.98	(1.95E+04)	(1.51E+03)	(3.88E+01)	0.14	(2.20E+04)	0.25	(10.38)
	APD	4.24					APD	2.15	APD	3.84	

calculated values of energy of vaporization obey the same trend as its observed value. The agreement is good for all the aforesaid systems, viz., (IV) and (V).

As per the analysis from Table 2, CED decreases with increase in the mole fractions of the first component for the systems (I), (II) and (V), whereas it increases with the increase in mole fractions of the first components for the systems (III), (IV), (VI) and (VII). Looking at the agreement between the observed and calculated CED, it is excellent for the systems (IV) and (V).

For the systems (I), (II) and (V), it is found that the solubility parameter decreases with the increase in mole fractions of the first components, whereas for the systems (III), (IV), (VI) and (VII), the solubility parameter values increase with the increase in the mole fractions of the first components. The agreement between observed and calculated values of solubility parameter is good for all the aforesaid systems and excellent for the systems (I), (IV) and (V).

From the results reported in Table 2, it is very obvious that the heat of vaporization decreases with the increase in mole fractions of the first components of the binary mixtures, whereas it increases with the increase in mole fraction of the first components of the binary mixtures undertaken. There is good agreement between the observed and computed values of heat of vaporization, for the systems (IV) and (V).

The results of Table 2 reveals that with increase in mole fractions of first component (acetonitrile), deviation from ideality in the internal pressure is observed, which is maximum in equimolar region. We can thus make an assumption that unlike interactions between acetonitrile and DMF is predominant. X–ray analysis reveals that the spread out DMF molecules are oriented randomly in pure liquid, while the simply shaped acetonitrile molecules rearrange their dipoles in antiparallel pairs in pure liquid.

The values of van der Waals constant, a, decrease with the increase in the mole fractions of first components for the systems (I), (IV), (V), (VI) and (VII), whereas an increase in its value is observed for the systems (II) and (III). The agreement between the two values of a is found to be good.

In conclusion, it may be said that the generalized hole theory developed recently yields quite successful results for the internal pressure, CED, solubility parameter, energy of vaporization, heat of vaporization and van der Waals constant in the case of seven binary mixtures, undertaken for the study in the present investigation.

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