

Thermodynamic interactions in binary mixtures of 1-chloronaphthalene and monocyclic aromatics

T M Aminabhavi^{*†}, Kamalika Banerjee & R H Balundgi

Chemistry Department, Karnatak University, Dharwad -580 003, India

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Thermodynamic interactions in binary mixtures of 1-chloronaphthalene with the monocyclic aromatics have been studied through calculation of excess molar volumes from Flory equation of state and that of Prigogine-Flory-Patterson theories using the experimental results of density, viscosity and speed of sound. The experimental excess viscosity has been compared with Bloomfield-Dewan theory, while the excess isentropic and isothermal compressibilities have been analysed using Benson-Kiyohara theory. Efforts have also been made to calculate the excess internal pressure from Prigogine-Saraga theory. All the excess quantities have been fitted to Redlich-Kister equation to estimate the binary coefficients and standard deviations.

Study of binary liquid mixtures containing 1-chloronaphthalene (1-CNP) has received considerable attention¹⁻⁶. However, binary mixtures of 1-chloronaphthalene with monocyclic aromatics such as benzene, methyl-benzene, 1,4-dimethylbenzene, 1,3,5-trimethylbenzene and methoxybenzene have not been studied earlier. Such mixtures are important from the viewpoint of understanding the intermolecular interactions. Herein, we present calculated values of excess molar volume, V^E , excess viscosity, $\ln \eta^E$, excess Gibbs energy of activation of flow, $G^{\star E}$, excess isentropic compressibility, k_s^E and excess isothermal compressibility, k_T^E obtained using reported data of density, ρ , viscosity, η , speed of sound, u and refractive index, n_D at 298.15 K, published earlier⁷. The results of k_s^E and k_T^E are compared with those calculated from Benson-Kiyohara⁸ as well as Flory theories^{9,10}. The experimental V^E values are compared with those obtained from Flory type calculations^{9,10} as well as Prigogine-Flory-Patterson (PFP) approach^{11,12}. Furthermore, the experimental excess viscosity data have been compared with those obtained theoretically from Bloomfield-Dewan theory¹³. The excess internal pressure, P_i^E and speed of sound have also been predicted from the Prigogine-Saraga equation¹⁴. The results of all the excess quantities are discussed in terms of the intermolecular interactions between mixing components.

Theoretical

Flory theory

Excess molar volume, V^E , has been calculated from the Flory equation of state^{9,10} as:

$$V^E = \left(\sum_{i=1}^2 x_i V_i^{\star} \right) \left(\tilde{V}^o^{7/3} / [4/3 - (\tilde{V}^o)^{1/3}] \right) (\tilde{T} - \tilde{T}^o) \quad \dots (1)$$

where $\tilde{V}^o$ is given by

$$\tilde{V}^o = \phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2 \quad \dots (2)$$

Here, $V_i^{\star} = \frac{V_i}{\tilde{V}_i}$ is the characteristic volume of the i -th

component in the mixture. Reduced volume, $\tilde{V}$ is calculated from thermal expansion coefficient, $\alpha \left[\equiv -(1/\rho)(\partial \rho / \partial T)_p \right]$ using relation:

$$\tilde{V} = \left[\frac{1 + (4/3)\alpha T}{(1 + \alpha T)} \right]^3 \quad \dots (3)$$

Reduced temperature, $\tilde{T}$ and the ideal reduced temperature, $\tilde{T}^o$ in Eq. (1) are calculated as:

$$\tilde{T}^o = \frac{(\tilde{V}^o)^{1/3} - 1}{\tilde{V}^o^{4/3}} \quad \dots (4)$$

The $\tilde{T}$ of the mixture is then calculated as:

$$\tilde{T} = \frac{(\phi_1 P_1^{\star} \tilde{T}_1 + \phi_2 P_2^{\star} \tilde{T}_2)}{(\phi_1 P_1^{\star} + \phi_2 P_2^{\star})} \quad \dots (5)$$

where the segment or hard-core volume fraction, ϕ_i

[†]e-mail: rrist@bgl.vsnl.net.in

Table 1—Values of molar volume (V), thermal expansion coefficient (α), heat capacity (C_p), isothermal compressibility (k_T), isentropic compressibility (k_S) and characteristic parameters (P^* , V^* and T^*) for pure liquids at 298.15 K

Liquid	V (cm ³ mol ⁻¹)	V^* (cm ³ mol ⁻¹)	$\tilde{V}$	T_c^a (K)	C_p^a (J.K ⁻¹ .mol ⁻¹)	$10^3\alpha$ (K ⁻¹)	k_S (TPa ⁻¹)	k_T (TPa ⁻¹)	$P^*.10^6$ (J.cm ⁻³)	T^* (K)
1-CNP	136.9	115.1	1.189	785.0	211.37	0.729	386	489	629	6313
Benzene	89.5	69.5	1.287	562.2	135.76	1.196	677	960	618	4754
Methylbenzene	107.0	85.0	1.258	591.8	157.29	1.051	676	900	551	5091
1,4-Dimethylbenzene	124.0	99.2	1.250	616.2	181.66	1.013	679	888	532	5194
1,3,5-Trimethylbenzene	139.7	110.7	1.262	637.3	209.10	1.073	647	876	582	5035
Methoxybenzene	109.3	88.2	1.240	645.6	208.57	0.962	504	649	680	5345

^aData taken from Riddick and Bunger, 1986.

is calculated as:

$$\phi_i = \frac{x_i V_i^*}{\sum_{i=1}^2 (x_i V_i^*)} \quad \text{and} \quad \phi_1 = 1 - \phi_2 \quad \dots (6)$$

The characteristic pressure, P^* is calculated using Eq. 7,

$$P^* = \frac{T \tilde{V}^2 \alpha}{k_T} \quad \dots (7)$$

where k_T is computed from isentropic compressibility, k_S and heat capacity, C_p of liquids using the relation:

$$k_T = k_S + T \alpha^2 V / C_p \quad \dots (8)$$

The values of α have been calculated from the experimental densities at different temperatures (see Table 1).

Prigogine-Flory-Patterson (PFP) theory

The PFP theory^{11,12} in the following form was used to compute V^E of the mixtures

$$\frac{V^E}{(x_1 V_1^* + x_2 V_2^*)} = - \frac{(\tilde{V}^{1/3} - 1) \tilde{V}^{2/3}}{[(4/3) \tilde{V}^{1/3} - 1]} \psi_1 \theta_2 \left(\frac{X_{12}}{P_1^*} \right) - \frac{(\tilde{V}_1 - \tilde{V}_2)^2 [(14/9) \tilde{V}^{1/3} - 1] \psi_1 \psi_2}{[(4/3) \tilde{V}^{1/3} - 1] \tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{(P_1^* \psi_2 + P_2^* \psi_1)} \psi_1 \psi_2 \quad \dots (9)$$

The first term of Eq. (9) represents the interactional contribution $\Delta(V_{int}^E)$ to V^E i.e., X_{12} parameter, often called contact interaction parameter; the second term is the difference in "free volume", ΔV_{fv}^E , while the third term is the internal pressure contribution (ΔV_{p^*}) i.e., p^* effect to V^E . In order to compute V^E from Eq. (9), we have used the values given in Table 1. The surface site fraction, θ_2 was calculated as:

$$\theta_2 = 1 - \theta_1 = \frac{\phi_2}{\left[\phi_2 + \phi_1 \left(\frac{V_2^*}{V_1^*} \right)^{1/3} \right]} \quad \dots (10)$$

and the contact energy fraction, ψ_i was calculated as:

$$\psi_1 = 1 - \psi_2 = \frac{x_1 P_1^* V_1^*}{\sum_{i=1}^2 (x_i P_i^* V_i^*)} \quad \dots (11)$$

Next, by following the Flory theory, excess enthalpy, H^E and excess free energy, G^E have been calculated using the following equations:

$$H^E = \sum_{i=1}^2 x_i P_i^* V_i^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + \frac{x_1 \theta_2 V_1^* X_{12}}{\tilde{V}} \quad \dots (12)$$

$$S^E = -3 \left[\frac{x_1 P_1^* V_1^*}{T_1^*} \ln \left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) + \frac{x_2 P_2^* V_2^*}{T_2^*} \ln \left(\frac{\tilde{V}_2^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) \right] \quad \dots (13)$$

$$G^E = \sum_{i=1}^2 x_i P_i^* V_i^* \left[\left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + 3 \tilde{T}_i \ln \left(\frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) \right] + \frac{x_1 \theta_2 V_1^* X_{12}}{\tilde{V}} \quad \dots (14)$$

Internal pressure

Internal pressure of liquids and liquid mixtures has been the subject of active interest in the literature¹⁵⁻¹⁷. Internal pressure, P_i can be estimated from the speed of sound data in conjunction with other thermodynamic parameters.

$$P_i = \frac{2^{1/6} RT}{2^{1/6} V - dN^{1/3} V^{2/3}} \quad \dots (15)$$

where V (m³/10⁻⁶.mol⁻¹), N (6.023×10²³ molecules/mole) and d (calculated in SI units) are

Table 2 — Comparison of experimental speed of sound ($u/\text{m}\cdot\text{s}^{-1}$) with those calculated from Benson-Kiyohara theory at 298.15 K

<i>1-Chloronaphthalene(1) + Benzene(2)</i>								
x_1	Expt	Theo	x_1	Expt	Theo	x_1	Expt	Theo
0.0000	1301	1219	0.3981	1359	1258	0.7973	1436	1288
0.0989	1309	1223	0.5035	1380	1268	0.8974	1456	1299
0.2022	1325	1234	0.5982	1398	1275	1.0000	1476	1309
0.3275	1346	1248	0.7022	1418	1284			
<i>1-Chloronaphthalene(1) + Methylbenzene(2)</i>								
x_1	Expt	Theo	x_1	Expt	Theo	x_1	Expt	Theo
0.0000	1310	1241	0.3973	1360	1265	0.7972	1440	1298
0.0995	1312	1242	0.4962	1380	1269	0.8918	1458	1301
0.1995	1327	1248	0.5970	1400	1278	1.0000	1476	1309
0.3037	1344	1256	0.6945	1420	1285			
<i>1-Chloronaphthalene(1) + 1,4-Dimethylbenzene(2)</i>								
x_1	Expt	Theo	x_1	Expt	Theo	x_1	Expt	Theo
0.0000	1311	1245	0.3991	1380	1278	0.7974	1440	1299
0.0966	1328	1256	0.4981	1395	1289	0.8991	1458	1302
0.1961	1346	1267	0.5970	1410	1291	1.0000	1476	1309
0.2964	1363	1277	0.7003	1424	1292			
<i>1-Chloronaphthalene(1) + 1,3,5-Trimethylbenzene(2)</i>								
x_1	Expt	Theo	x_1	Expt	Theo	x_1	Expt	Theo
0.0000	1340	1263	0.3988	1387	1291	0.8017	1445	1304
0.0983	1350	1272	0.4984	1401	1292	0.9016	1460	1305
0.2041	1362	1279	0.6008	1416	1300	1.0000	1476	1309
0.2992	1374	1282	0.6999	1430	1306			
<i>1-Chloronaphthalene(1) + Methoxybenzene(2)</i>								
x_1	Expt	Theo	x_1	Expt	Theo	x_1	Expt	Theo
0.0000	1416	1296	0.3974	1435	1296	0.7827	1456	1300
0.0985	1420	1295	0.4997	1440	1299	0.8985	1466	1306
0.1969	1425	1300	0.5959	1445	1300	1.0000	1476	1309
0.2977	1430	1298	0.6962	1450	1301			

respectively, molar volume, Avogadro number and molecular diameter; R is molar gas constant in SI units and T is temperature in Kelvin. Values of d needed to calculate P_i from Eq.(15) were calculated using the following semiempirical relation^{17,18}:

$$d^{5/2} = \frac{1}{7.21 \times 10^{19}} \cdot \frac{V\gamma^{1/4}}{T_C^{1/4}} \quad \dots (16)$$

where γ ($\text{N}\cdot\text{m}^{-1}$) is surface tension and T_C (in Kelvin) is critical temperature. Surface tension of liquids or their mixtures is related to speed of sound through the relation¹⁷⁻²⁰:

$$\gamma = 6.3 \times 10^{-4} \rho u^{3/2} \quad \dots (17)$$

where ρ ($\text{kg}\cdot\text{m}^{-3}$) is density and u ($\text{m}\cdot\text{s}^{-1}$) is speed of sound. T_C of the mixture was obtained from the following additive relation:

$$\frac{1}{T_{C(\text{mix})}} = \sum_{i=1}^2 \frac{\Phi_i}{T_{C(i)}} \quad \dots (18)$$

where $\phi [= x_i V_i / \sum_{i=1}^2 (x_i V_i)]$ is the volume fraction.

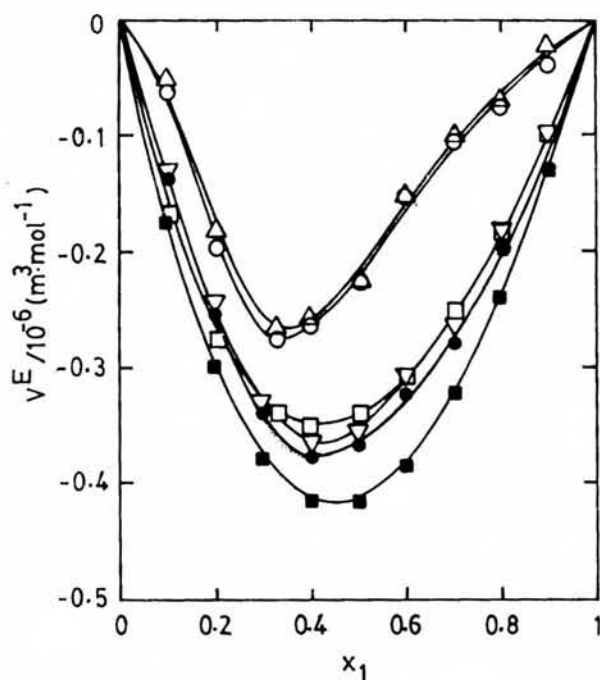
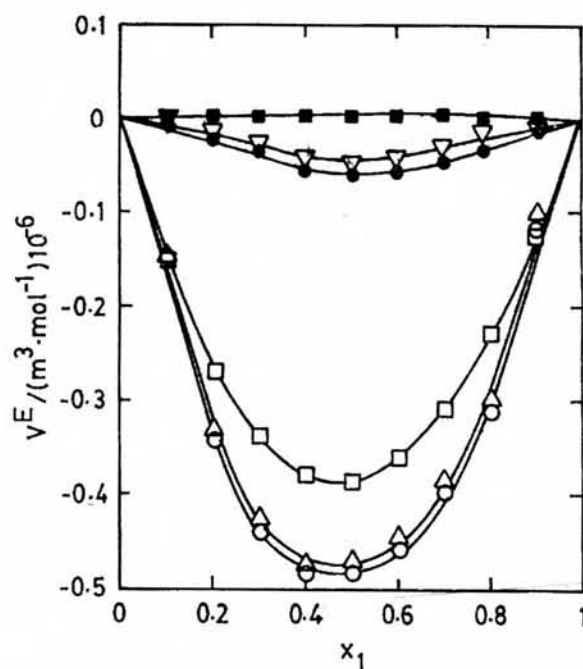
Bloomfield-Dewan theory

Viscosity of binary liquid mixtures has been studied extensively over the past several decades^{21,22}. Several empirical correlations have been proposed to study the deviations in viscosity of liquid mixtures that generally require adjustable parameters. However, the most commonly used equation to predict the viscosity deviation is:

$$\ln \eta^E = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad \dots (19)$$

Table 3 — Comparison of near equimolar excess molar volume data with the theoretical calculations at 298.15 K for 1-CNP + monocyclic aromatics

1-CNP with aromatics	θ_2	$X_{12}/(\text{J.mol}^{-1})$ from V^E	$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$			PFP contribution from		
			Expt	Flory	PFP	int	fv	ip
Benzene	0.413	10.3	-0.212	-0.341	-0.222	0.127	0.311	-0.038
Methylbenzene	0.454	2.77	-0.351	-0.390	-0.354	0.037	0.170	-0.221
1,4-Dimethylbenzene	0.379	5.87	-0.308	-0.417	-0.311	0.076	0.135	-0.252
1,3,5-Trimethylbenzene	0.495	-5.73	-0.471	-0.387	-0.472	-0.085	0.227	-0.160
Methoxybenzene	0.456	-3.98	-0.046	0.002	-0.047	-0.048	0.097	0.098

Fig. 1 — Comparison of V^E data for mixtures of 1-CNP+benzene; symbols: (O) expt; (Δ) PFP theory, (●) Flory theory and for mixtures of 1-CNP + 1,4-dimethylbenzene; Symbols: (●) expt, (∇) PFP theory, (■) Flory theory at 298.15 KFig. 2 — Comparison of V^E data for mixtures of 1-CNP + 1,3,5-trimethylbenzene; symbols: (O) expt; (Δ) PFP theory, (●) Flory theory and for mixtures of 1-CNP + methoxybenzene; symbols: (●) expt, (∇) PFP theory, (■) Flory theory at 298.15 K

In order to calculate $\ln \eta^E$ theoretically, Bloomfield and Dewan¹³ proposed an equation that does not require any adjustable parameters and which correlates viscosity of the mixture with the thermodynamic properties of pure components. This theory is based on free volume and absolute reaction rate concepts^{21,22} as well as Flory equation without any numerical adjustment. The Bloomfield-Dewan equation is given as¹³:

$$\ln \eta^E_{th} = \ln \eta_G + \ln \eta_{fv} \quad \dots (20)$$

where $\ln \eta_G$ and $\ln \eta_{fv}$ are respectively, the contributions from free energy and free volume effects. Eq.(20) may further be rewritten by splitting the $\ln \eta_G$ term into enthalpy and entropy contributions:

$$\ln \eta^E_{th} = \ln \eta_H + \ln \eta_S + \ln \eta_{fv} = -G^E / RT + \ln \eta_{fv} \quad \dots (21)$$

By splitting G^E into enthalpy and entropy contributions we get,

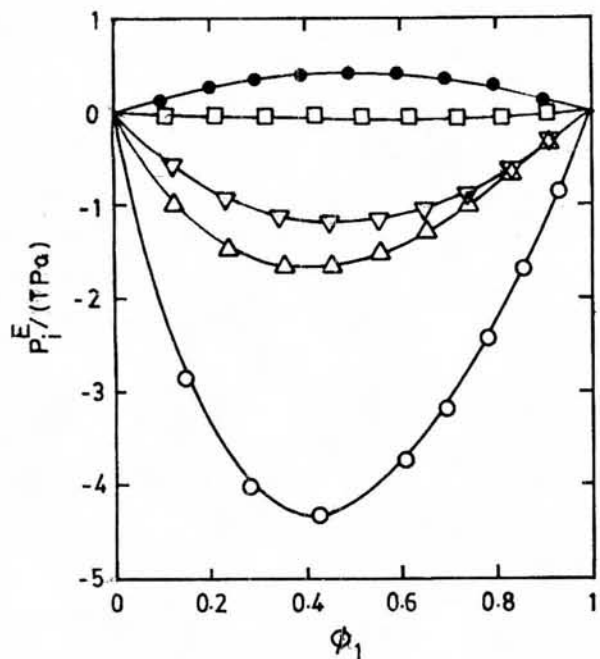
$$\ln \eta^E_{th} = -H^E / RT + S^E / R + \left[\frac{1}{\bar{V} - 1} - \left(\sum_{i=1}^2 \frac{x_i}{(\bar{V}_i - 1)} \right) \right] \quad \dots (22)$$

In order to calculate $\ln \eta^E_{th}$, the experimental H^E values were taken from Grolier *et al.*¹ and the values of S^E have been calculated from Eq.(13). The free volume contribution to $\ln \eta^E$ was then calculated in the usual manner from Flory theory.

Using the theory of Eyring²², we have calculated the excess molar Gibbs energy of activation for the

Table 4—Calculated values of H^E , G^{*E} and $\partial V^E/\partial T$ for the binary mixtures of 1-CNP with monocyclic aromatics at near equimolar compositions

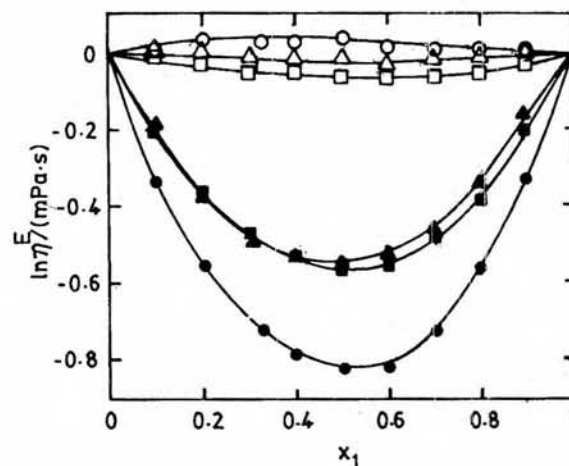
1-CNP +	x_1	H^E (J/mol)	G^{*E} (J/mol)	$10^3 \cdot \partial V^E/\partial T$ ($10^{-6} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}$)
Benzene	0.5035	197.6	323.7	-0.896
Methylbenzene	0.4962	43.5	129.5	-1.339
1,4-Dimethylbenzene	0.5970	133.3	183.8	-1.316
1,3,5-Trimethylbenzene	0.4984	-209.5	-39.7	-1.721
Methoxybenzene	0.4997	-126.7	-39.43	-0.279

Fig. 3—Excess internal pressure vs volume fraction at 298.15K for the mixtures of 1-CNP + (O) benzene, 1-CNP + (Δ) methylbenzene, 1-CNP + ($\square$) 1,4-dimethylbenzene, 1-CNP + ($\bullet$) 1,3,5-trimethylbenzene and 1-CNP + (∇) methoxy benzene.

viscous flow, G^{*E} as:

$$G^{*E} = RT(\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \quad \dots (23)$$

where η and V are respectively, the viscosity and molar volume of the mixture; η_i and V_i represent the respective quantities of component i in the mixture and RT has the usual meaning. It may be noted that G^{*E} is a kinetic energy barrier impeding the attainment of the minimum level of a free energy corresponding to thermodynamic equilibrium. However, it is possible to split this contribution between enthalpy or entropy, i.e., H^{*E} or S^{*E} which could be obtained from the temperature dependence of G^{*E} . Such H^{*E} or S^{*E} values referring to activation energy (kinetics) cannot be fundamentally

Fig. 4—Plots of $\ln \eta^E$ vs mole fraction calculated for Bloomfield, Dewan equation for mixtures of 1-CNP with ($\bullet$) benzene (Δ) methylbenzene and ($\blacksquare$) 1,4-dimethylbenzene with those of experimental $\ln \eta^E$ for the same mixtures (unfilled symbols).

replaced by H^E or S^E obtained from thermodynamic equilibrium (discussed earlier).

Benson-Kiyohara theory

Ultrasonic data of the mixtures have been used²³⁻²⁶ to calculate excess isothermal compressibility, k_T^E and deviations in isentropic compressibility, k_S^E . The values of k_S^E have been calculated from Benson-Kiyohara equation⁸ using:

$$k_S^E = k_S^{\text{mix}} - k_S^{\text{ideal}} \quad \dots (24)$$

Here, the ideal isentropic compressibility term was computed using the relation:

$$k_S^{\text{ideal}} = k_{S,1} \Phi_1 + k_{S,2} \Phi_2 + T \left\{ \Phi_1 V_1 \alpha_1^2 / C_{P,1} + \Phi_2 V_2 \alpha_2^2 / C_{P,2} - \frac{V^{\text{ideal}} (\alpha^{\text{ideal}})^2}{C_P^{\text{ideal}}} \right\} \quad \dots (25)$$

The values of $C_{P,i}$ for the individual components of the mixtures are taken from the work of Riddick *et al*²⁷. In the absence of C_P data for mixtures of 1-CNP

Table 5 — Experimental and computed values of $\ln \eta^E$ Bloomfield-Dewan equation at 298.15 K for near equimolar compositions

1-CNP with	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_{IV}$	$\ln \eta_{th}^E$	$\ln \eta_{exp}^E$	$(\ln \eta_{exp}^E - \eta_{th}^E)$
Benzene	-0.859	-0.053	0.088	-0.825	0.038	0.864
Methylbenzene	-0.588	-0.037	0.075	-0.550	-0.016	0.534
1,4-Dimethylbenzene	-0.567	-0.028	0.032	-0.562	-0.062	0.500
1,3,5-Trimethylbenzene	-0.666	-0.071	-0.185	-0.756	-0.030	0.726
Methoxybenzene	-0.432	-0.038	0.022	-0.449	-0.018	0.043

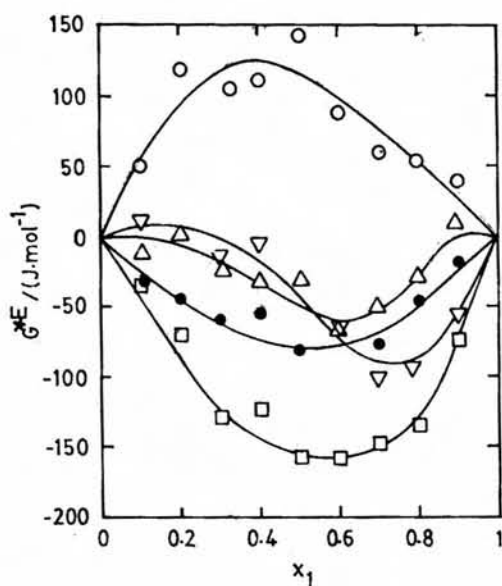


Fig. 5 — Excess molar Gibbs energy of activation of flow vs mole fraction at 298.15 K for the same mixtures as presented in Fig. 3.

+ benzenes, the following additive relation was used:

$$C_p = x_1 C_{p1} + x_2 C_{p2} \quad \dots (26)$$

The individual component C_p data were taken from Table 1.

Isenthalpic compressibility from Flory theory

The experimental value of k_T as given by Eq.(8) to calculate the deviation in isothermal compressibility, k_T^E may be expressed as:

$$k_T^E = k_T^{mix} - k_T^{ideal} \quad \dots (27)$$

where the k_T^{mix} and k_T^{ideal} terms are computed from Eq.(8). The term k_T^{ideal} is calculated as :

$$k_T^{ideal} = \Phi_1 k_{T1} + \Phi_2 k_{T2} \quad \dots (28)$$

We have also attempted to compute k_T from Flory theory^{9,10}. A survey of the literature indicates that very few attempts^{28,29} have been made to predict k_T^E using Flory theory as given below.

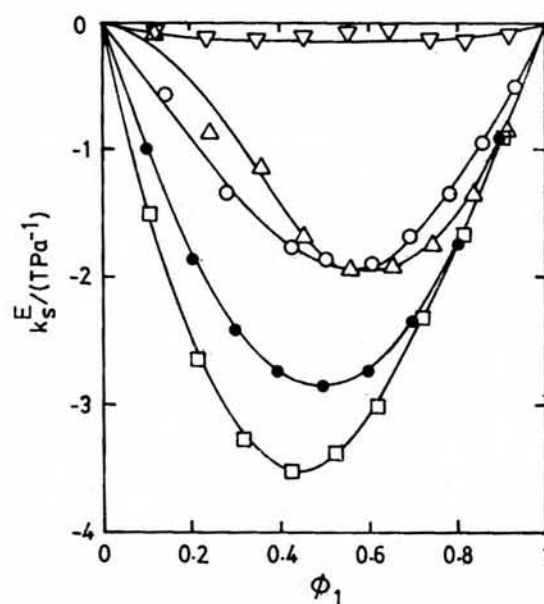


Fig. 6 — Excess isentropic compressibility calculated from Benson-Kiyohara theory at 298.15 K for the same mixtures with the symbols as in Fig. 3.

$$k_T^E = \frac{3\tilde{V}^2}{R^* \left[(\tilde{V}^{1/3} - 1)^{-1} - 3 \right]} - \frac{\sum_{i=1}^2 (\Phi_i \tilde{V}_i k_{T,i})}{\tilde{V}} \quad \dots (29)$$

The required parameters for the calculation of k_T^E were taken from Table 1.

Prigogine-Saraga theory

In order to judge the validity of speed of sound data, we have also computed theoretically the values of u from Prigogine-Saraga theory^{14,30} by rearranging Eq.(17) as:

$$u = [\gamma 10^4 / 6.3 \rho]^{2/3} \quad \dots (30)$$

where γ is surface tension. In order to calculate u in $m.s^{-1}$, the input values of γ and ρ were taken in the c.g.s. units.

$$\gamma = \gamma^* \tilde{\gamma} \quad \dots (31)$$

where γ^* and $\tilde{\gamma}$ are the characteristic and reduced surface tension, respectively. According to Patterson

Table 6—Estimated parameters of excess functions for the binary mixtures

Function	Temp/K	A_0	A_1	A_2	σ
<i>1-Chloronaphthalene(1) + Benzene(2)</i>					
$V^E/10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-0.921	-0.683	0.384	0.030
$\ln \eta^E/(\text{mPa} \cdot \text{s})$	298.15	0.099	0.0974	0.028	0.008
$G^E/(\text{J} \cdot \text{mol}^{-1})$	298.15	448	254	81.1	20.1
$10^6 \cdot P_i^E/(\text{TPa})$	298.15	-16.8	-6.3	-3.06	-0.031
$k_S^E/(\text{TPa}^{-1})$	298.15	-76.0	18.6	23.26	0.448
<i>1-Chloronaphthalene(1) + Methylbenzene(2)</i>					
$V^E/10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-1.40	-0.330	-0.567	0.024
$\ln \eta^E/(\text{mPa} \cdot \text{s})$	298.15	0.096	0.046	0.118	0.007
$G^E/(\text{J} \cdot \text{mol}^{-1})$	298.15	-190.3	108.6	279	16.8
$10^6 \cdot P_i^E/(\text{TPa})$	298.15	-6.47	-2.85	-5.35	0.019
$k_S^E/(\text{TPa}^{-1})$	298.15	-75.0	49.7	28.67	1.05
<i>1-Chloronaphthalene(1) + 1,4-Dimethylbenzene(2)</i>					
$V^E/10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-1.467	-0.308	0.025	0.013
$\ln \eta^E/(\text{mPa} \cdot \text{s})$	298.15	-0.244	0.105	-0.027	0.005
$G^E/(\text{J} \cdot \text{mol}^{-1})$	298.15	-619.5	253.6	-67	11.1
$10^6 \cdot P_i^E/(\text{TPa})$	298.15	-0.258	0.120	-0.457	0.014
$k_S^E/(\text{TPa}^{-1})$	298.15	-137.7	-39.5	8.17	0.455
<i>1-Chloronaphthalene(1) + 1,3,5-Trimethylbenzene(2)</i>					
$V^E/10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-2.00	-0.201	0.260	0.023
$\ln \eta^E/(\text{mPa} \cdot \text{s})$	298.15	-0.100	0.010	-0.020	0.005
$G^E/(\text{J} \cdot \text{mol}^{-1})$	298.15	-282.6	21.8	-45.9	11.8
$10^6 \cdot P_i^E/(\text{TPa})$	298.15	1.69	-0.034	-0.27	0.011
$k_S^E/(\text{TPa}^{-1})$	298.15	-114.6	-7.06	8.12	0.152
<i>1-Chloronaphthalene(1) + Methoxybenzene(2)</i>					
$V^E/10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$	298.15	-0.236	0.052	0.187	0.002
$\ln \eta^E/(\text{mPa} \cdot \text{s})$	298.15	-0.092	0.164	-0.1896	0.008
$G^E/(\text{J} \cdot \text{mol}^{-1})$	298.15	-160.6	421.1	-488.8	20.7
$10^6 \cdot P_i^E/(\text{TPa})$	298.15	-4.76	-6.45	-6.42	0.005
$k_S^E/(\text{TPa}^{-1})$	298.15	-3.60	-13.2	12.9	0.174

and Rastogi³¹, the γ^* is related to the state parameters as:

$$\gamma^* = k^{1/3} \cdot T^{*1/3} \cdot P^{*2/3} \quad \dots (32)$$

where k is the Boltzmann constant. Following Prigogine and Saraga¹², the equation for reduced surface tension is

$$\tilde{\gamma} = M \tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^2} \ln \left[\frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1} \right] \quad \dots (33)$$

where M is fractional decrease in the nearest neighbours of a cell due to migration from bulk phase to the surface phase and its value varies from 0.25 to 0.29 for a closely packed lattice. In the present calculations, we have used $M = 0.25$. The calculated values of u from Eq.(30) are compared with the experimental results in Table 2.

Results and Discussion

The excess molar volumes have been calculated from the experimental densities of liquids and liquid mixtures using the equation,

$$V^E = V_m - V_1 x_1 - V_2 x_2 \quad \dots (34)$$

where V_m is molar volume of binary mixture calculated as $V_m = (M_1 x_1 + M_2 x_2) / \rho_m$; ρ_m is mixture density; and $V_1 (= M_1 / \rho_1)$ and $V_2 (= M_2 / \rho_2)$ are the molar volumes of components 1 and 2; M_1 , ρ_1 and M_2 , ρ_2 are the molecular weights and densities of components 1 and 2 respectively. The equimolar experimental V^E values are compared with the V^E values calculated from Flory and PFP theories at 298.15 K in Table 3. It is observed that in all the cases, the V^E values are negative and compare well with the PFP V^E values rather than with the Flory V^E values. However, the results presented in Fig.1 are

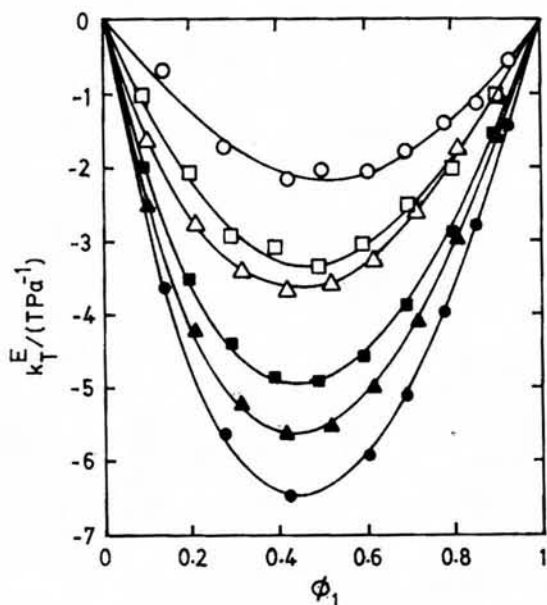


Fig. 7 — Comparison of experimental excess isothermal compressibility with those of Flory theory for mixtures of 1-CNP + benzene: symbols (O) expt, (●) Flory; 1-CNP + 1,4-dimethylbenzene: symbols (Δ) expt, (▲) Flory; and 1-CNP + 1,3,5-trimethylbenzene: symbols (□) expt, (■) Flory.

compared for only two typical mixtures, viz., 1-CNP + benzene and 1-CNP + 1,4-dimethylbenzene at 298.15 K. Similar data are presented in Fig. 2 for the mixtures of 1-CNP + 1,3,5-trimethylbenzene and 1-CNP + methoxybenzene at 298.15 K. It can be seen that the values of thermal expansivity, α and isothermal compressibility, k_T for 1-CNP are lower than those for other liquids (Table 1). Thus, when it is mixed with aromatic liquids having increasing number of methyl-groups, the binary mixtures exhibit large free volume effects. This explains the observed increased values of V^E with increasing number of methyl groups on benzene moiety. The calculated values of H^E and G^E for all the mixtures except those of 1-CNP + 1,3,5-trimethylbenzene or 1-CNP + methoxybenzene are positive suggesting order creation in these mixtures. This is attributed to (i) π - π interactions between 1-CNP and monocyclic aromatics (except those containing 1,3,5-trimethylbenzene or methoxybenzene). This is further supported by the fact that the values of second order mixing quantities, i.e., $\partial V^E / \partial T$ are negative for all the mixtures (Table 4) suggesting that there is a short-range orientational order effect between 1-CNP and the monocyclic aromatic molecules. When two plate like molecules are mixed, the order is created due to a regular alignment, but such an order might possibly be

destroyed whenever the bulky methoxy group is present (as in methoxybenzene).

The PFP contribution terms due to interactional, free volume and internal pressure along with θ_2 and X_{12} terms are also included in Table 3. In the original PFP theory, the interactional term is positive in the absence of H-bond and other specific interactions. However, for the mixtures of 1-CNP + 1,3,5-trimethylbenzene or 1-CNP + methoxybenzene, the PFP interactional contribution terms are negative. Since the interactional term is dominant in H^E , the negative values of H^E for these mixtures are responsible for giving the negative values of the interactional terms. Similarly, the G^E terms follow the same signs as those of H^E as shown in Table 4. However, the free volume terms are positive in all the cases, whereas the internal pressure contribution term is negative in all the mixtures except 1-CNP + methoxybenzene. This further supports the fact that the internal pressure (P^*) term often dominates V^E , particularly if one of the components has a higher P^* value and lower α than the other. This situation leads to negative V^E with negative H^E . This is indeed the case for 1-CNP + methoxybenzene system. It may further be noted that even the values of X_{12} for the mixtures 1-CNP + 1,3,5-trimethylbenzene and 1-CNP + methoxybenzene are negative which parallel the negative values of internal pressure contribution observed for these mixtures. In view of the nonavailability of H^E data for the present mixtures, the X_{12} values have been calculated using the experimental V^E data at 298.15 K as:

$$X_{12} = \frac{1}{(\phi_1 \theta_2 \tilde{T}(X_{12}))} \left[\sum \phi_i R_i^* (\tilde{T}(X_{12}) - \tilde{T}_i(X_{12})) \right] \quad \dots (35)$$

The values of X_{12} thus calculated are positive for all the mixtures except those of 1-CNP + 1,3,5-trimethylbenzene and 1-CNP + methoxybenzene mixtures (Table 3).

The values of excess internal pressure, P_i^E calculated from the difference between the mixture and individual components using Eqs (15-18) based on volume fraction, Φ_1 , of 1-CNP are presented in Fig. 3. It is found that for 1-CNP + 1,3,5-trimethylbenzene, the P_i^E values are positive while the negative values are observed for the remaining mixtures except 1-CNP + 1,4-dimethylbenzene for which P_i^E values are almost independent of mixture composition. Such negative values indicate that the repulsive forces between the interacting molecules

have a predominant effect for those mixtures exhibiting positive values of P_1^E and thus, indicating that the attractive forces are greater than the repulsive interactions. The excess internal pressure decreases considerably for mixtures of 1-CNP + benzene as evidenced by a large negative value when compared to 1-CNP + 1,3,5-trimethylbenzene, for which the P_1^E values are positive.

The calculated values of $\ln \eta^E$ from the Bloomfield and Dewan equation are compared with those of the experimentally calculated values in Table 5. The enthalpy, entropy and free volume contribution terms, viz., $\ln \eta_H$, $\ln \eta_S$ and $\ln \eta_V$ to viscosity are also listed. The differences between the experimental and predicted values of $\ln \eta^E$ for all the mixtures are quite larger than that for 1-CNP + methoxybenzene. However, for the mixtures the signs of the experimentally calculated and theoretically predicted values of $\ln \eta^E$ are identical except in case of 1-CNP + benzene mixture. Similarly, the experimental and theoretical $\ln \eta^E$ curves for 1-CNP + methoxybenzene and 1-CNP + 1,3,5-trimethylbenzene are presented in Fig. 4. The agreement between theory and experiment is again poor. Such differences between theoretical and experimental quantities are attributed to: (i) the over estimation of the entropy contribution, i.e., S^E/R term determined from the free volume difference and (ii) use of the calculated H^E data instead of experimental measurements.

The results of free energy of activation of flow, G^{*E} are presented in Fig. 5 and these curves do not exhibit any systematic dependence on the size of the aromatic molecules in the binary mixtures. The plots of k_S^E calculated from Eq. (24) are presented in Fig. 6. Higher negative values are observed for all the binaries except 1-CNP + methoxybenzene (for which there is no dramatic dependence of k_S^E on Φ_1). In Fig. 7 are compared the predicted values of k_T^E from Benson -Kiyohara theory with those computed from the experimental data for a few representative systems, viz., 1-CNP + benzene, 1-CNP + 1,4-dimethylbenzene and 1-CNP + 1,3,5-trimethylbenzene. In all the cases, the k_T^E values are negative and larger deviations are observed between the predicted and experimental curves for 1-CNP+benzene when compared to 1-CNP+1,4-dimethylbenzene or 1-CNP + 1,3,5-trimethylbenzene.

The values of excess functions viz., V^E , $\ln \eta^E$, G^{*E} , P_1^E and k_S^E have been fitted to Redlich Kister Equation (32) of the type:

$$V^E \text{ (or } Y^E) = C_1 C_2 \sum_{j=1}^{k=3} A_{j-1} (C_2 - C_1)^{j-1} \dots (36)$$

to estimate the parameter values of A_0 , A_1 , A_2 along with the standard deviations, σ and these are compiled in Table 6.

In conclusion, the present approach is an attempt to understand the agreement between the well established theoretical predictions and the experimentally calculated quantities which are frequently used in the study of binary liquid mixtures. The results presented here will be useful to gain a better understanding of the mixing phenomena in binary mixtures.

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