

The values of excess Gibbs function calculated as per Goats⁶ *et al.* for the system benzene and cyclohexane at the eutectic point is found to be 344 J/mole. This is in very good agreement with the value reported in Table 1. Thus the values recorded in Table 1 are reliable.

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Weak Interactions in Binary Mixtures of Chlorobenzene & Bromobenzene with *o*-, *m*- & *p*-Xylenes

R. K. NIGAM & N. N. MAINI

Chemistry Department, Kurukshetra University*
Kurukshetra

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Surface tension, dielectric constant and NMR data for the mixtures of chlorobenzene and bromobenzene with *o*-, *m*- and *p*-xylenes have been obtained. Analysis of these results has confirmed the existence of weak specific interactions in these mixtures.

ANALYSIS of thermodynamic excess functions for binary liquid mixtures has been reported earlier¹⁻⁶ with a view to demonstrating the presence of weak specific interactions in them. The weak specific interactions in the title mixtures have now been supported by studies of such properties as surface tension, dielectric constants, IR, UV and NMR spectroscopy.

Chlorobenzene, bromobenzene, *o*-, *m*- and *p*-xylenes were purified and their purity checked in the manner described elsewhere¹⁻⁵.

Surface tension and dielectric constant for pure components and mixtures were determined using methods already described⁷⁻⁹.

IR and UV spectra for pure components and their mixtures were recorded on Beckman IR-20 and Beckman DU-2 spectrophotometers respectively. The proton resonance spectra were recorded on a Varian HR60 spectrophotometer using cyclohexane as an internal standard.

Based on Telang's calculations¹⁰, Palit¹¹ deduced the following expression for viscosity of liquids (η), interrelating the viscosity, surface tension (γ) and density (ρ).

$$\log \eta M = ZN^{1/2} \cdot 3.03 RT [\gamma(M/\rho)^{2/3}] + \phi(1/\rho) \dots (1)$$

*Present address: Professor and Head of the Chemistry Department, Rohtak University, Rohtak.

where $Z = 1.091$ for cubic packing, $N =$ Avogadro's number, $\phi(1/\rho)$ a function of specific volume, $M =$ molecular weight of the liquid, and R the gas constant. This equation can be extended for binary mixtures. Taking the variation of $\phi(1/\rho)$ with temperature to be very small, the plot of $\log \eta M$ against $\gamma(M/\rho)^{2/3}/T$ should be linear with a constant slope of 0.481 for all liquids having cubical packing. Using this equation for binary mixtures the plot of $\log \eta_{\text{mix}} (x_1 M_1 + x_2 M_2)$ against γ_{mix}

$$\left(\frac{x_1 M_1 + x_2 M_2}{\rho_{\text{mix}}} \right)^{2/3} / T$$

should also be linear with the same slope having cubic packing for the mixtures. For the mixtures of chlorobenzene and bromobenzene with *o*-, *m*- and *p*-xylenes, the viscosity data were taken from our earlier communication⁶, the plots of $\log \eta_{\text{mix}} (x_1 M_1 + x_2 M_2)$ versus $\gamma_{\text{mix}} \left(\frac{x_1 M_1 + x_2 M_2}{\rho_{\text{mix}}} \right)^{2/3} / T$ were linear.

The slopes of linear plots calculated by least square method at 25°, 30° and 35° mixtures are given below:

	Slope
Chlorobenzene + <i>o</i> -xylene	0.92
Chlorobenzene + <i>m</i> -xylene	1.80
Chlorobenzene + <i>p</i> -xylene	3.40
Bromobenzene + <i>o</i> -xylene	1.24
Bromobenzene + <i>m</i> -xylene	1.42
Bromobenzene + <i>p</i> -xylene	1.25

It is evident from above that the values of slope for these mixtures do not correspond to a value 0.481 as it should be for pure liquids and their mixtures if association possibilities are ruled out in them. The plot of η_{mix} against composition show a small negative deviation. The result of excess thermodynamic properties of these mixtures suggested that the amount of complex formation goes on increasing from *ortho* through *meta* to *para*-xylenes in the case of mixtures with chlorobenzene and *ortho* through *para* to *meta*-xylenes in case of mixtures with bromobenzene. The order of increase in slopes also follow the same sequence. It can, therefore, be said that deviation in slope from ideal value 0.481 is a measure of the existence of weak specific interactions resulting in the formation of new species in the mixtures as reported by Palit (unpublished).

This fact is further substantiated by the analysis of surface tension data in the light of statistical theories of surface tensions of mixtures based on cell model theory due to Prigogine¹², Prigogine-Englert Chowles¹³ and Bellemans and Stecki¹⁴. In these theories if we adjust the parameter θ in the manner reported elsewhere, and γ_{mix} values are computed for the mixtures, the values are found in very good agreement with the corresponding experimental values. This manner of adjusting θ takes automatically the deviations from combining rule (from geometric mean for interaction energies) and also the existence of weak specific interactions in the mixtures.

The data in Table 1 (only representative data at 30° for various systems are given) which show good agreement between experiment and theory, provides

TABLE 1 — COMPARISON OF CALCULATED AND OBSERVED γ_{mix} AT DIFFERENT COMPOSITIONS (30°)

Mole fraction of chlorobenzene	γ_{mix} (dynes/cm)			Mole fraction of bromobenzene	γ_{mix} (dynes/cm)		
	Obs.	Bellemans	Englert-Chowles		Obs.	Bellemans	Englert-Chowles
CHLOROENZENE + <i>o</i> -XYLENE				BROMOENZENE + <i>o</i> -XYLENE			
0.1	29.27	29.35	28.83	0.1	29.66	29.56	29.11
0.2	29.53	29.63	28.71	0.2	30.29	30.05	29.27
0.4	30.10	30.21	28.82	0.4	31.57	31.15	29.96
0.5	30.43	30.51	29.07	0.5	32.11	31.74	30.49
0.7	31.22	31.14	29.92	0.7	33.13	33.00	31.93
0.9	31.91	31.79	31.27	0.9	34.41	34.37	33.91
CHLOROENZENE + <i>m</i> -XYLENE				BROMOENZENE + <i>m</i> -XYLENE			
0.1	27.97	27.94	27.32	0.1	28.26	28.11	27.57
0.2	28.39	28.34	27.24	0.2	28.96	28.71	27.74
0.4	29.34	29.19	27.53	0.4	30.32	30.54	28.57
0.5	29.86	29.64	27.91	0.5	31.07	30.77	29.23
0.7	30.84	30.59	29.13	0.7	32.76	32.37	31.05
0.9	31.71	31.60	30.98	0.9	34.38	34.14	33.57
CHLOROENZENE + <i>p</i> -XYLENE				BROMOENZENE + <i>p</i> -XYLENE			
0.1	27.87	27.69	26.97	0.1	28.03	27.86	27.21
0.2	28.41	28.11	26.83	0.2	28.82	28.47	27.32
0.4	29.37	29.01	27.08	0.4	30.33	29.84	28.10
0.5	29.79	29.48	27.47	0.5	31.09	30.60	28.77
0.7	30.68	30.49	28.80	0.7	32.70	32.26	30.70
0.9	31.65	31.56	30.84	0.9	34.30	34.10	33.42

evidence for the existence of weak specific interaction in accordance with the analysis of excess properties of the mixtures.

Dielectric constant data (Table 2) for mixtures can be used to calculate⁹ the apparent polarization of one component on assuming the molar polarization of other component equal to the value for the pure liquid. From the plots of calculated apparent polarization against the composition of mixtures, it is observed that molar polarization increases, abruptly at infinite dilution in *o*-, *m*- and *p*-xylenes. This indicates the complexing tendency of chlorobenzene and bromobenzene with *o*-, *m*- and *p*-xylenes. On analysing the dielectric polarization data of these mixtures in the manner described elsewhere⁹, it is observed that contact pairs are exclusively formed in these mixtures.

The result of UV and IR spectra for these mixtures have not been of any help in deciding about the occurrence of weak specific interaction, in conformity with the observations recorded earlier¹⁵. However, large shift of NMR signal of methyl protons of xylenes in their solutions with chlorobenzene and bromobenzene is indicative of complex formation between halobenzenes and xylenes. Only representative data for the systems chlorobenzene-*o*-xylene and bromobenzene-*o*-xylenes are given in Table 3 for brevity (the data for other system can be had from the author on request). On analysing the NMR data it is observed that interactions between xylenes with chlorobenzene and bromobenzene are primarily electrostatic in nature and the complex formed in each mixture is rather very weak.

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TABLE 2 — DIELECTRIC POLARIZATION STUDIES OF BINARY MIXTURES AT 25°

Mole fraction of chlorobenzene or bromobenzene	Dielectric constant	Density d_m	P_{12} cc	P_A cc
CHLOROENZENE + <i>o</i> -XYLENE				
0.1417	3.099	0.9065	58.55	85.67
0.3188	3.451	0.9440	51.48	70.82
0.3778	3.627	0.9575	52.88	70.12
0.4762	3.804	0.9785	53.86	66.44
0.5723	4.155	1.0000	56.24	66.57
0.6655	4.507	1.0220	58.18	66.10
0.7554	4.824	1.0430	59.59	65.14
0.8969	5.283	1.0780	61.01	63.15
BROMOENZENE + <i>o</i> -XYLENE				
0.1397	3.092	0.961	48.34	80.12
0.2774	3.205	1.041	48.89	66.83
0.3756	3.522	1.098	52.06	68.08
0.4718	3.742	1.156	53.74	66.41
0.5649	4.029	1.212	55.88	66.24
0.6604	4.346	1.273	57.85	65.78
0.7404	4.600	1.325	59.18	65.06
0.8345	4.854	1.385	60.31	63.86
0.9135	5.108	1.437	61.37	63.16

 TABLE 3 — PROTON RESONANCE SHIFT (δ) OF CHLOROENZENE AND BROMOENZENE IN *o*-XYLENE RELATIVE TO PURE HALOENZENE

Mole fraction of chlorobenzene	δ ppm	Mole fraction of bromobenzene	δ ppm
0.1845	0.36	0.3305	1.34
0.4880	1.14	0.5060	2.46
0.6532	2.88	0.5447	2.46
0.7428	3.36	0.7375	3.72
0.9120	3.78	0.8951	3.94

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Effective Debye Temperature of Liquids on the Basis of Quasi-crystalline Structure

J. D. PANDEY

Department of Chemistry, University of Allahabad
Allahabad 211002

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The effective Debye temperature (θ) of liquid argon, oxygen, nitrogen, methane, and neon has been calculated as a function of temperature and pressure using ultrasonic velocity and isothermal compressibility data. The values of θ decrease by increasing temperature while increase by increasing the pressure.

A NUMBER of theoretical and experimental evidences¹⁻¹⁰ are available in support of the quasi-crystalline behaviour of the liquid. By assuming the quasi-crystalline model Joshi¹¹, Mitra *et al.*¹² and Jain *et al.*¹³ evaluated the Debye temperature of water utilizing the data given by Singwi and Sjolander⁵. Recently Kor *et al.*^{14,15} calculated the effective Debye temperature of water, methanol, ethanol, carbon tetrachloride and toluene as a function of temperature and pressure assuming the atomic motions in these liquids as similar to those in solids. These authors utilized the ultrasonic absorption data for their calculations. By applying the quasi-crystalline model to the cryogenic liquids argon, nitrogen, oxygen, neon and methane, the present author has extended the calculation of effective Debye temperature as a function of temperature and pressure.

The following sets of equation^{14,15} have been utilized to evaluate the Debye temperature (θ) of liquids:

$$\theta = \frac{h}{k} \left[\frac{9N}{4\pi v} \left(\frac{2}{c_i^3} + \frac{1}{c_1^3} \right) \right]^{1/3} \quad \dots(1)$$

$$\frac{1}{c_1^3} + \frac{2}{c_i^3} = (\rho\beta_{T,\infty})^{3/2} \left[2 \left\{ \frac{2(1+\sigma)}{3(1-2\sigma)} \right\}^{3/2} + \left\{ \frac{(1+\sigma)}{3(1-\sigma)} \right\}^{3/2} \right] \quad \dots(2)$$

$$\sigma = \frac{3A-2}{6A+2}, A = \left(\frac{K_{T,\infty}}{G_{T,\infty}} \right) = \left(\frac{K_{T,\infty}}{K_{T,r}} \right) \left(\frac{\eta_V}{\eta_S} \right) \left(\frac{\tau_S}{\tau_V} \right) \quad \dots(3)$$

$$\frac{\eta_V}{\eta_S} = \frac{4}{3} \left(\frac{\alpha \text{ expt}}{\alpha \text{ class}} - 1 \right) \quad \dots(4)$$

$$\tau_S = \frac{4}{3} \eta_S \beta_0, K_{T,r} = \frac{1}{\beta_{T,r}} = G_{T,\infty} \frac{\eta_V}{\eta_S}, G_{T,\infty} = \frac{\eta_S}{\tau_S}$$

$$\eta_V = K_{T,r} \tau_V \text{ and } \frac{1}{K_{T,\infty}} = \beta_{T,\infty} = \beta_0 - \beta_{T,r} \quad \dots(5)$$

Here all the symbols have their usual notations¹⁶. Previous workers have evaluated the value of θ using the above relation and have utilized the experimental data for shear viscosity η_S , density ρ ultrasonic absorption α/f^2 and velocity c . In the present case a simplified procedure has been used which avoids the use of absorption and viscosity.

From Eq. (5),

$$\frac{K_{T,\infty}}{K_{T,r}} = \frac{K_{T,\infty}}{K_{T,0}} - 1 = \frac{1}{\gamma} - 1 \quad \dots(6)$$

where $K_{T,\infty}$, $K_{T,0}$ and γ are respectively the isothermal bulk modulus, adiabatic bulk modulus and ratio of the heat capacities. Again,

$$\frac{\tau_S}{\tau_V} = \frac{4}{3} \frac{\eta_S}{\eta_V} \cdot \beta_{T,0} K_{T,r} = \frac{4}{3} \frac{\eta_S}{\eta_V} \cdot \frac{K_{T,\infty}}{K_{T,0} - K_{T,\infty}} \quad \dots(7)$$

Hence,

$$\frac{\tau_S \eta_V}{\tau_V \eta_S} = \frac{4}{3} \left(\frac{1}{1-\gamma} \right) \quad \dots(8)$$

Using Eqs. (6) and (8), one gets,

$$A = \frac{4}{3} \cdot \frac{1}{\gamma} \quad \dots(9)$$

Thus we need only ρ , γ and $\beta_{T,\infty}$ for evaluating the values θ for liquids.

The effective Debye temperatures for liquid argon, liquid oxygen, nitrogen, methane and neon were calculated using Eqs. (1), (2), (3) and (9). The data needed for the calculations were taken from different sources¹⁷⁻²¹. In Table 1, are recorded the calculated values of θ for different liquids at different temperatures and pressures. It is observed that θ decreases by increasing the temperature at constant pressure for argon and neon. For liquid oxygen, nitrogen and methane both the temperature and pressure, have been varied and it has been found that the pressure has marked effect on the effective Debye temperature for liquid oxygen, nitrogen, and methane. The increase of pressure results in an increase in the value of θ , although the increase is not so abrupt. For N₂ at 113.6°K, the effective Debye temperature increases only by 2.5°K for an increase of 21.1 kg/cm² pressure.

The results of the calculation show that the effective Debye temperature has reasonable value for all the liquids investigated. The temperature dependence of effective Debye temperature in the present case is similar to that of other workers¹⁴. The order of θ values and their temperature