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Density & Refractive Index Increments & Excess Molar Volumes of Binary Liquid Mixtures

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Density and refractive index increments, and excess molar volumes on ten sets of binary mixtures at 20°C have been predicted from the theoretical relations proposed. Volume changes on mixing have been accounted through the binary interaction parameters. The experimental data are discussed in terms of thermodynamic interactions and the nature of reacting species.

The literature concerning excess properties of liquid mixtures has been exhaustive after the pioneering work of Prigogine[1] in the early fifties. Since then a number of theories have been proposed and tested on binary mixtures. However, no theory yet appears to predict two other important quantities namely, density and refractive index increments of mixtures. In this paper, we present a useful phenomenological theory to predict density and refractive index increments of solvent mixtures. The theory is simple and experimentally less demanding to test; all that is needed is to measure the densities and refractive indices of pure components and their mixtures over the full range of composition. Volume changes during mixing could be accounted from the binary contact parameters[2].

Theory

To develop the formalism the relations (1) and (2) suggested earlier[3] for changes of volume and refractivity, respectively are considered.

$$\Delta V_{mix}=\left(\sum_{i=1}^{2} N_i V_i\right) A_{12}\varphi_1\varphi_2 \qquad \ldots (1)$$

$$\Delta R_{mix}=\left(\sum_{i=1}^{2} N_i V_i\right) B_{12}\varphi_1\varphi_2 \qquad \ldots (2)$$

Here, the parameters A_{12} and B_{12} represent changes in volume and refractivity respectively, during mixing. These parameters are functions of composition of the mixture; $\varphi_1[\equiv X_i V_i/(X_1V_1+X_2V_2)]$ is the volume fraction of the ith component. V_i, N_i and X_i represent the volume, number of mol and mol fraction of the ith component. The density, ρ, and polarizability, P, of the mixture may be expressed in terms of A_{12} and B_{12} as

$$\rho=(\varphi_1\rho_1+\varphi_2\rho_2)/(1+A_{12}\varphi_1\varphi_2) \qquad \ldots (3)$$

$$P=(P_1\varphi_1+P_2\varphi_2+B_{12}\varphi_1\varphi_2)/(1+A_{12}\varphi_1\varphi_2) \qquad \ldots (4)$$

Conventional derivation from Eqs (3) and (4) leads to density and refractive index increments, represented by Eqs (5) and (6) respectively.

$$\left(\frac{d\rho}{d\varphi_1}\right)_{P,T} = \frac{(\rho_1-\rho_2)-\rho\left[A_{12}(\varphi_2-\varphi_1)+\frac{dA_{12}}{d\varphi_1}(\varphi_1\varphi_2)\right]}{(1+A_{12}\varphi_1\varphi_2)} \qquad \ldots (5)$$

$$\left(\frac{dn}{d\varphi_1}\right)_{P,T} = \frac{(n^2+2)^2\left\{\left[(P_1-P_2)+B_{12}(\varphi_2-\varphi_1)+\frac{dB_{12}}{d\varphi_1}(\varphi_1\varphi_2)\right]-P\left[A_{12}(\varphi_2-\varphi_1)+\frac{dA_{12}}{d\varphi_1}(\varphi_1\varphi_2)\right]\right\}}{6n\,(1+A_{12}\varphi_1\varphi_2)} \qquad \ldots (6)$$

The values of A_{12}, and their derivatives, $dA_{12}/d\varphi_1$ and $dB_{12}/d\varphi_1$ may be obtained from the equations suggested earlier[4]. All calculations were done on a DCM microcomputer.

Results and Discussion

In view of the availability of our own data[5] on ten sets of binary mixtures at 20°C further experimentation to test the validity of Eqs (5) and (6) appeared unnecessary. Excess molar volumes for all these mixtures have been calculated using[6] the relation (7)

$$V^E=\frac{M_1\varphi_1+M_2\varphi_2}{\rho}-\frac{M_1\varphi_1}{\rho_1}-\frac{M_2\varphi_2}{\rho_2} \qquad \ldots (7)$$

where M_1 and M_2 are the molecular weights of individual components of the mixture. The values of V^E were then fitted to the quadratic equation of type (8) to estimate the coefficients A, B and C

$$V^E = \varphi_1\varphi_2 [A + B(\varphi_2 - \varphi_1) + C(\varphi_2 - \varphi_1)^2] \quad \ldots (8)$$

The quantity $V^E/\varphi_1\varphi_2$ together with A, B and C as obtained from Eq. (8) is presented in Table 1 for all systems. Also included in Table 1 are the refractive index increments calculated using Eq. (6) for yellow, green and blue wavelengths of mercury, and the density increments calculated from Eq. (5). It is interesting to note that excess molar volumes are negative for three systems namely, bromobenzene(1)-acetophenone(2), acetophenone(1)-chlorobenzene(2) and carbon tetrachloride(1)-chlorobenzene(2), suggesting specific interactions between the mixing species. However, positive values are observed for rest of the systems except water(1)-dimethyl sulphoxide(2) wherein a reversal of sign occurs with increase in concentration of water in the mixture. The critical composition being $\varphi_1 \simeq 0.5$. It appears that at low water concentrations in the mixture weak complexes are formed and destroyed in the higher concentration region. Excess molar volume is the highest for systems, DMSO(1)-bromobenzene(2) and benzene(1)-bromobenzene(2); its dependence on φ_1 shows a steeper minima for the latter than the former. A linear dependence is observed for benzene(1)-acetophenone(2); on the other hand, benzene(1)-chlorobenzene(2) exhibits positive deviations.

Density increments are negative for six systems namely, benzene(1)-acetophenone(2), acetophenone(1)-chlorobenzene(2), DMSO(1)-bromobenzene(2), water(1)-DMSO(2), benzene(1)-chlorobenzene(2) and benzene(1)-bromobenzene(2). The system benzene(1)-bromobenzene(2) exhibits the highest negative values than the rest while the smallest negative values are observed for the system acetophenone(1)-chlorobenzene(2). The dependence of density increment on φ_1 in the case of water(1)-DMSO(2) is anomalous (Fig. 1). A linear dependence of $(d\rho/d\varphi_1)_{P,T}$ is seen for acetophenone(1)-chlorobenzene(2), benzene(1)-acetophenone(2), benzene(1)-chlorobenzene(2) and acetophenone(1)-toluene(2) (Fig. 1). However, for DMSO(1)-bromobenzene(2) and benzene(1)-bromobenzene(2) systems, positive deviations are seen while for bromobenzene(1)-chlorobenzene(2), CCl_4(1)-chlorobenzene(2) and bromobenzene(1)-acetophenone(2) negative deviations are observed. Furthermore, no correlation in the sign or magnitude of $(d\rho/d\varphi_1)_{P,T}$ could be possible with $V^E/\varphi_1\varphi_2$.

Refractive index increment being an optical quantity appears to have some correlation (atleast in its sign) with that of density increment. Systems with negative values of $(dn/d\varphi_1)_{P,T}$ at all wavelengths also exhibit negative values for $(d\rho/d\varphi_1)_{P,T}$, except CCl_4(1)-chlorobenzene(2) mixture. The large positive

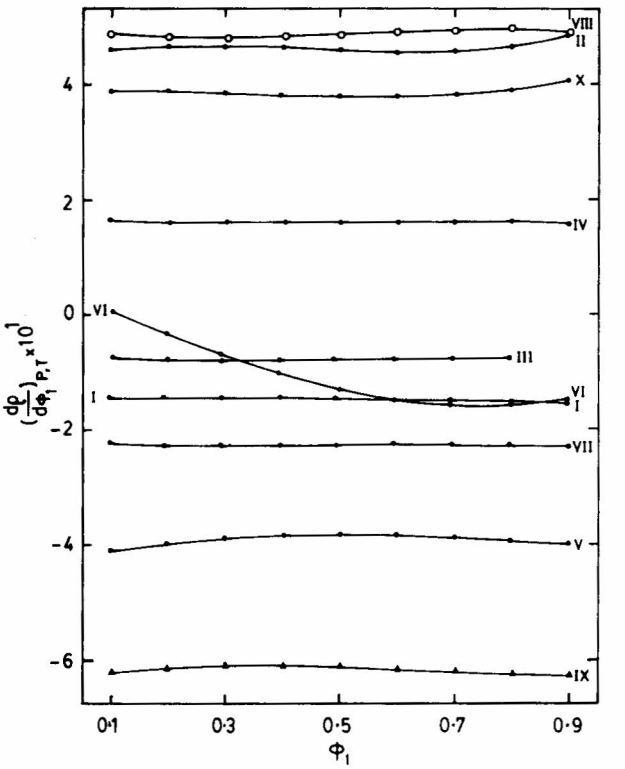

Fig. 1—Dependence of density increment on φ_1 for binary systems I-X (see Table 1)

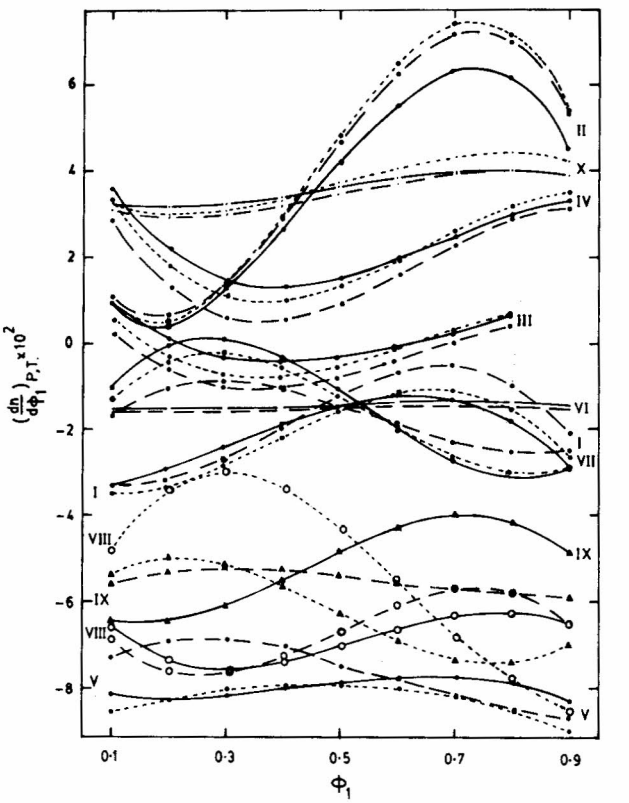

Fig. 2—Dependence of refractive index increment on φ_1 for binary systems I-X (see Table 1) [● — ● at 589 nm; ● --- ● at 546 nm; and ---- at 436 nm]

Table 1—Excess Volumes, Density and Refractive Index Increments and Computed Parameters of Eq. (8) for Binary Systems at 20°C

Volume fraction (φ_1)	$V^E/\varphi_1\varphi_2$	Density increment $\left(\frac{d\rho}{d\varphi_1}\right)_{P,T}$	Refractive index increment $\left(\frac{dn}{d\varphi_1}\right)^y_{P,T}$	$\left(\frac{dn}{d\varphi_1}\right)^s_{P,T}$	$\left(\frac{dn}{d\varphi_1}\right)^b_{P,T}$
		(I) Benzene(1)-acetophenone(2)			
		A = 3.7825; B = 0.08749; C = −0.07			
0.1004	3.8077	−0.14685	−0.03307	−0.03311	−0.03517
0.1962	3.8098	−0.14674	−0.02956	−0.03221	−0.03351
0.2948	3.8066	−0.14669	−0.02458	−0.02724	−0.02874
0.3975	3.7975	−0.14687	−0.01910	−0.01978	−0.02221
0.4948	3.7834	−0.14741	−0.01476	−0.01254	−0.01618
0.5991	3.7624	−0.14854	−0.01225	−0.00672	−0.01169
0.6947	3.7378	−0.15021	−0.01297	−0.00503	−0.01093
0.7977	3.7056	−0.15280	−0.01811	−0.00915	−0.01536
0.8991	3.6681	−0.15626	−0.02876	−0.02122	−0.02673
		(II) Bromobenzene(1)-acetophenone(2)			
		A = −3.4634; B = −1.7389; C = 1.6370			
0.1019	−3.8102	0.4619	0.008829	0.01074	0.009385
0.2009	−3.9178	0.4665	0.006079	0.006654	0.005678
0.2991	−3.8978	0.4664	0.01313	0.01408	0.01388
0.4005	−3.7447	0.4632	0.02663	0.02915	0.02997
0.4993	−3.4659	0.4591	0.04197	0.04660	0.04837
0.5996	−3.0521	0.4564	0.0557	0.06249	0.06496
0.6961	−2.5297	0.4576	0.0634	0.07169	0.07438
0.7974	−1.8500	0.4658	0.0616	0.07028	0.07247
0.8968	−1.0525	0.4841	0.04454	0.05319	0.055396
		(III) Acetophenone(1)-chlorobenzene(2)			
		A = −1.1775; B = −0.3219; C = −0.5717			
0.1048	−1.7891	−0.07402	0.008718	0.002282	0.005591
0.1988	−1.5789	−0.07783	0.001262	−0.006031	−0.003014
0.2963	−1.4036	−0.07973	−0.002959	−0.010036	−0.007261
0.3957	−1.2695	−0.08010	−0.004270	−0.010349	−0.007748
0.4941	−1.1814	−0.07947	−0.003292	−0.007991	−0.005489
0.5450	−1.1370	−0.07838	−0.000671	−0.003954	−0.001473
0.6970	−1.1394	−0.07739	0.002878	0.0006113	0.003154
0.7969	−1.1880	−0.07708	0.006479	0.004393	0.007078
		(IV) Acetophenone(1)-toluene(2)			
		A = 1.4816; B = 0.07345; C = −0.3693			
0.1008	1.3049	0.1641	0.03596	0.02868	0.03379
0.2025	1.3946	0.1619	0.02225	0.01316	0.01835
0.3028	1.4532	0.1609	0.01521	0.006185	0.01109
0.4051	1.4823	0.1606	0.01335	0.005670	0.01008
0.5039	1.4811	0.1607	0.01531	0.009620	0.01348
0.6036	1.4506	0.1610	0.01971	0.01614	0.01950
0.7002	1.3930	0.1609	0.02503	0.02306	0.02614
0.8004	1.3042	0.1603	0.03025	0.02894	0.03203
0.9011	1.1851	0.1587	0.03378	0.03148	0.03505
		(V) Dimethyl sulphoxide(1)-bromobenzene(2)			
		A = 10.6612; B = 0.3219; C = 0.8374			
0.1010	11.4513	−0.4139	−0.08159	−0.07286	−0.08558
0.2019	11.1507	−0.4004	−0.08236	−0.06928	−0.08295
0.3031	10.9178	−0.3912	−0.08174	−0.06882	−0.08087
0.4054	10.7520	−0.3859	−0.08038	−0.07076	−0.07959
0.5047	10.6582	−0.3842	−0.07872	−0.07498	−0.07947
0.6029	10.6304	−0.3854	−0.07781	−0.07807	−0.08006
0.7039	10.6691	−0.3890	−0.07765	−0.08212	−0.08221
0.8034	10.7742	−0.3946	−0.07903	−0.08536	−0.08580
0.8984	10.9363	−0.4015	−0.08226	−0.08714	−0.09080

(Contd.)

Table 1—Excess Volumes, Density and Refractive Index Increments and Computed Parameters of Eq. (8) for Binary Systems at 20°C—*Contd.*

Volume fraction (φ_1)	$V^E/\varphi_1\varphi_2$	Density increment $\left(\frac{d\rho}{d\varphi_1}\right)_{P,T}$	Refractive index increment $\left(\frac{dn}{d\varphi_1}\right)^y_{P,T}$	$\left(\frac{dn}{d\varphi_1}\right)^s_{P,T}$	$\left(\frac{dn}{d\varphi_1}\right)^b_{P,T}$
		(VI) Water(1)-dimethyl sulphoxide(2) A = 0.8578; B = −5.189; C = −0.5858			
0.1022	−3.6420	+0.004654	−0.1577	−0.1590	—
0.1973	−2.4988	−0.03447	−0.1563	−0.1580	—
0.2951	−1.3673	−0.07130	−0.1523	−0.1557	—
0.3955	−0.2524	−0.10390	−0.1467	−0.1526	—
0.4976	0.8329	−0.1302	−0.1408	−0.1493	—
0.5968	1.8406	−0.1479	−0.1362	−0.1469	—
0.6951	2.7937	−0.1572	−0.1344	−0.1463	—
0.7976	3.7392	−0.1574	−0.1375	−0.1488	—
0.8974	4.6126	−0.1472	−0.1468	−0.1558	—
		(VII) Benzene(1)-chlorobenzene(2) A = 2.8263; B = −0.3678; C = 0.7591			
0.0990	2.0431	−0.2235	−0.01043	−0.01689	−0.01303
0.1964	2.3231	−0.2271	−0.00052	−0.01059	−0.00408
0.2965	2.5509	−0.2284	+0.001298	−0.00876	−0.00219
0.3977	2.7193	−0.2281	−0.00299	−0.01038	−0.00567
0.4958	2.8239	−0.2272	−0.01073	−0.01409	−0.01224
0.5970	2.8691	−0.2263	−0.01969	−0.01871	−0.01997
0.6953	2.8542	−0.2262	−0.02727	−0.02288	−0.02663
0.7967	2.7772	−0.2273	−0.03141	−0.02554	−0.03045
0.8981	2.6379	−0.2303	−0.02936	−0.02526	−0.02906
		(VIII) Carbon tetrachloride(1)-chlorobenzene(2) A = −1.6736; B = −0.5656; C = −1.0387			
0.1017	−2.7834	0.4880	−0.06590	−0.06876	−0.04849
0.2033	−2.3750	0.4823	−0.07364	−0.07599	−0.03377
0.3074	−2.0456	0.4810	−0.07575	−0.07630	−0.02990
0.4044	−1.8198	0.4827	−0.07403	−0.07260	−0.03398
0.5028	−1.6705	0.4863	−0.07033	−0.06682	−0.04323
0.6008	−1.6018	0.4905	−0.06623	−0.06115	−0.05520
0.7013	−1.6143	0.4938	−0.06317	−0.05753	−0.06797
0.7971	−1.7043	0.4944	−0.06265	−0.05784	−0.07778
0.9008	−1.8877	0.4903	−0.06537	−0.06502	−0.08510
		(IX) Benzene(1)-bromobenzene(2) A = 7.74; B = −1.1481; C = 1.7889			
0.0992	7.9692	−0.6234	−0.06460	−0.05616	−0.05418
0.1993	7.6966	−0.6148	−0.06483	−0.05350	−0.04998
0.2995	7.5673	−0.6110	−0.06113	−0.05229	−0.05154
0.4003	7.5822	−0.6108	−0.05515	−0.05267	−0.05648
0.4985	7.7366	−0.6129	−0.04875	−0.05395	−0.06293
0.5994	8.0390	−0.6164	−0.04323	−0.05575	−0.06938
0.6990	8.4804	−0.6203	−0.04043	−0.05757	−0.07383
0.7981	9.0604	−0.6241	−0.04185	−0.05898	−0.07463
0.8993	9.7978	−0.6273	−0.04899	−0.05960	−0.06999
		(X) Bromobenzene(1)-chlorobenzene(2) A = 1.4087; B = −1.3068; C = 1.1019			
0.0994	1.0691	0.3902	0.03262	0.03132	0.03240
0.2016	1.0213	0.3886	0.03191	0.02967	0.03021
0.2989	1.0614	0.3852	0.03260	0.03009	0.03091
0.3977	1.1875	0.3811	0.03419	0.03190	0.03350
0.4977	1.4027	0.3776	0.03624	0.03448	0.03711
0.5987	1.7096	0.3764	0.03826	0.03718	0.04083
0.7024	2.1182	0.3794	0.03971	0.03929	0.04366
0.8000	2.5895	0.3879	0.04005	0.04002	0.04490
0.8995	3.1563	0.4044	0.03883	0.03878	0.04250

values of $(dn/d\varphi_1)_{P,T}$ for CCl_4-ClC_6H_5 may be attributed to large difference in densities of the two components. Refractive index difference is large ($\Delta n \simeq 0.06$) for CCl_4 and bromobenzene, nevertheless negative values of refractive index increments are observed at all the three wavelengths. This may be due to the strong electronic perturbation between the components of the mixture[4]. Three other systems which need special attention are: bromobenzene(1)-acetophenone(2), bromobenzene(1)-chlorobenzene(2) and acetophenone(1)-toluene(2) wherein we observe positive values for both density and refractive index increments. Dependence of $(dn/d\varphi_1)_{P,T}$ on φ_1 for all the mixtures studied is shown in Fig. 2. It can be clearly seen that the refractive index increment depends on the wavelength selected. An S-type dependence is seen in majority of systems with an inversion taking place around the middle of the composition scale ($\varphi_1 \simeq 0.5$). The only system for which a linear behaviour is seen is water(1)-DMSO(2) mixture. The blue line could not be measured for this system within the scale range of the refractometer used. Probably, similar dependence could also be predicted for blue wavelength. However, to arrive at firm conclusions, more number of systems need to be studied to predict the dependence of both density and refractive index increments on composition of the mixture. Clearly much more needs to be done to correlate the component behaviour and their interactions in mixtures in relation to the quantities proposed in this study.

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