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Evaluation of Internal pressure of Multicomponent Liquid Mixtures Using Velocity and Density Data

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Abstract. An empirical relationship between internal pressure (P_{int}) ultrasonic velocity (u) and density (ρ) has been suggested. This relation can be used to compute directly internal pressure from the experimental values of velocity and density. The proposed relation has been tested for four binary, four ternary and three quarternary liquid nixtures. The results are discussed in terms of average percentage deviation (APD). A satisfactory agreement has been found.

1. Introduction

In liquid state cohesive forces are of primary importance. Different liquid systems differ essentially in their relative degree of cohesion and this cohesion creates a pressure directed inwards such that the dissolved solute experiences this inwards pressure of 10^3 to 10^4 atm. Thus, the internal pressure which is the resultant of forces of attraction and repulsion between the constituents in the liquid medium, provides the estimate of pressure directed inward by cohesion. However, a detailed study of internal pressure was brought by Hildebrand and Scott[1,2] and subsequently by several workers[3-10]. For binary liquid mixtures, it has been used to investigate molecular interaction[6-7, 11-13]. Internal pressure of liquids and mixtures can be computed either from the knowledge of the viscosity, density and ultrasonic velocity[4] or from the experimental values of thermal expansion coefficient and isothermal compressibility. Theoretical deduction of internal pressure of binary liquid mixtures was carried out by Subrahmanyam et al[8] using Flory statistical theory. Due to the lack of experimental data of these parameters beyond binaries, the internal pressure could not be estimated for multicomponent liquid systems. In the present communication an empirical relationship between internal pressure, ultrasonic velocity and density has been suggested. In the proposed empirical relation, the internal pressure is expressed in terms of ultrasonic velocity, density and temperature of the liquid systems. The validity of the relation has been tested for four binary, four ternary and three quaternary liquid systems at 298.15K. The calculated values of internal pressure for all the systems are compared with the experimental ones and percentage deviations were calculated. A fairly good agreement was found.

Key-words: Internal pressure, ultrasonic velocity, empirical relation, multicomponent liquid systems, average percentage deviation.

2. Proposed Relation

Thermodynamically, the internal pressure of a liquid P_{int} is given by

$$(\frac{\partial U}{\partial V})_T = P_{int} = T(\frac{\partial P}{\partial T})_V - P$$

i.e.

$$P_{int} = \frac{\alpha T}{\beta_T} - P \tag{1}$$

where P is the external pressure, α the coefficient of thermal expansion, β_T the isothermal compressibility and T the temperature. At zero pressure the above equation reduces to

$$P_{int} = \frac{\alpha T}{\beta_T} \tag{2}$$

Empirical relations for α and β_T in terms of velocity, density and temperature has been proposed by one of us[14].

These relations are as follows:

$$\alpha = (75.6 \times 10^{-3})/(T^{1/9} u^{1/2} \rho^{1/3}) \text{ deg}^{-1} \tag{3}$$

$$\beta_T = (17.1 \times 10^{-4})/(T^{4/9} u^2 \rho^{4/3}) \, cm^2 \text{ dyne}^{-1} \tag{4}$$

where u, ρ and T are expressed respectively in ms^{-1}, g, cm^{-3} and K. These empirical relations were tested for a number of liquid systems including pure liquids, binary, ternary and quaternary liquid mixtures. From equations (2), (3) and (4), we have

$$P_{int} = 44.2 \times T^{4/3} u^{3/2} \rho \tag{5}$$

here P_{int} is expressed in dyne cm^{-2}.

The above equation is very useful in the sense that internal pressure of a liquid system can be computed directly from the experimental values of density and velocity. It can also be used to estimate P_{int} in the case of liquid mixtures. If the mixture be an ideal and non-interacting, the ideal value of P_{int}, i.e. $(P_{int})_{idl}$ is given by

$$(P_{int})_{idl} = \sum_{i=1}^{n} x_i (P_{int_i}$$

where x_i is the mole fraction and $(P_{\text{int}})_i$ the internal pressure of the i^{th} component in a n-component liquid mixture. Again, from equation (2), the internal pressure of real liquid mixture, $(P_{\text{int}})_m$, is given by

$$(P_{\text{int}})_m = \frac{\alpha_m T}{(\beta_T)_m} = 44.2\, T^{4/3}\, u_m^{3/2}\, \rho_m \tag{7}$$

Here α_m and $(\beta_T)_m$ are the thermal expansivity and isothermal compressibility of mixture. Internal pressure for various liquid systems has been deduced as:

(i) Internal pressure computed from equation (5) is denoted by $(P_{\text{int}})_{\text{theo}}$.

(ii) Internal pressure deduced from equation (6), where $(P_{\text{int}})_i$ is the experimental value of internal pressure of i^{th} component in the n-component liquid system, is denoted by $(P_{\text{int}})_{idl-\text{exp}}$.

(iii) Internal pressure deduced from equation (6), where $(P_{\text{int}})_i$ is the computed value of internal pressure from equation (5) of i^{th} component in the *n*-component liquid system, is denoted by $(P_{\text{int}})_{idl-\text{theo}}$.

3. Results and Discussion

Four binary, four ternary and three quaternary liquid system undertaken for the present investigations are: cyclohexane + benzene (I), n-hexane + cyclohexane (II), n-hexane + benzene (III), n-decane + cyclohexane (IV); cyclohexane + n-heptane + toluene (V), toluene + n-heptane + n-hexane (VI), n-pentane + n- hexane + benzene (VII), n-hexane + cyclohexane + benzene (VIII); n-pentane + toluene + n-heptane + cyclohexane (IX), n-decane + n- hexane + cyclohexane + benzene (X) and n-pentane + n-hexane + benzene + toluene (XI). Thus, systems (I) to (IV) are binary, (V) to (VIII) ternary and (IX) to (XI) quaternary. Ultrasonic velocity, density and internal pressure of pure liquid components at 298.15K are recorded in table 1. Experimentally determined values[10,15] of velocity and density as function of mole fractions for various systems are reported in tables 2-12 at 298.15K. In all the tables the values of ρ, u and P_{int} are expressed respectively in gcm^{-3}, ms^{-1} and 10^{12} $dyne\ cm^{-2}$, The empirical equation (5) has been employed to compute the values of internal pressure for all the systems and denoted as $(P_{\text{int}})_{\text{theo}}$. Equation (6) has been used to compute the $(P_{\text{int}})_{\text{idl-exp}}$ values. With the help of equations (5), (6) and (7) $(P_{\text{int}})_{\text{idl-theo}}$ values for all the liquid systems have also been computed. The values of internal pressure obtained from equation (6) as $(P_{\text{int}})_{\text{idl-exp}}$ and $(P_{\text{int}})_{\text{idl-}theo}$ are compared and the agreement is found to be quite satisfactory.

The average percentage deviation (APD) for all the systems are given below. The following table concludes that there is good agreement between $(P_{int})_{idl-exp}$ and $(P_{int})_{idl-theo}$ and the results obtained by the proposed empirical relation are quite satisfactory. The APD values ranges from 2.2 to 5.1 except one value 9.5 in the case of system (VII).

Systems	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
APD	3.9	5.1	5.0	2.2	3.3	4.2	9.5	4.4	3.3	3.4	3.5

Table 1. Parameters for pure liquid components

Liquids	u	P	P_{int}
Benzene	1295.00	0.8731	3.7817
Toluene	1304.00	0.8627	3.4769
Cyclohexane	1253.00	0.7733	3.1778
n-Pentane	990.00	0.6216	2.6359
n-hexane	1075.00	0.6552	2.5800
n-heptane	1131.00	0.6791	2.6359
n-decane	1224.00	0.7262	2.6919

Table 2. Internal pressure of binary liquid mixture (I) Cyclohexane (x_1) + Benzene (x_2)

x_1	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	% P
0.7128	1255.87	0.7883	3.089	3.307	3.176	4.0
0.6481	1257.73	0.7934	3.116	3.346	3.214	3.9
0.5965	1259.70	0.7975	3.139	3.377	3.244	3.9
0.5798	1260.07	0.8000	3.150	3.387	3.254	3.9
0.4847	1260.85	0.8072	3.182	3.443	3.310	3.9
0.4512	1261.98	0.8109	3.200	3.463	3.330	3.8
0.4089	1262.42	0.8159	3.222	3.489	3.355	3.8
0.3586	1260.50	0.8212	3.235	3.519	3.385	3.8
0.3095	1263.86	0.8262	3.268	3.548	3.414	3.8
0.2609	1264.50	0.8311	3.290	3.577	3.442	3.8
					APD	3.9

Table 3. Internal pressure of binary liquid mixture (II) n-hexane (x_1) + Cyclohexane (x_2)

x_1	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	% P
0.7634	1245.18	0.6766	2.617	2.424	2.276	6.1
0.6702	1247.07	0.6853	2.657	2.511	2.365	5.8
0.5903	1248.61	0 6971	2.708	2.586	2.441	5.6
0.5365	1250.98	0.7013	2.732	2.636	2.493	5.4
0.4469	1251.34	0.7105	2.769	2.720	2.579	5.2
0.3691	1257.43	0.7191	2.823	2.792	2.653	5.0
0.2942	1254.09	0.7304	2.856	2.862	2.725	4.8
0.1220	1257.52	0.7393	2.902	3.023	2.890	4.4
0.1504	1257.60	0.7470	2.933	2.996	2.862	4.5
0.0682	1258.35	0.7584	2.980	3.073	2.941	4.3
					APD	5.1

Table 4. Internal pressure of binary liquid mixture (III) n-hexane (x_1) + Benzene (x_2)

x_1	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	% P
0.1599	1260.34	0.8184	3.224	3.488	3.349	4.0
0.2174	1257.50	0.8034	3.154	3.400	3.260	4.1
0.2798	1257.34	0.7874	3.091	3.305	3.164	4.3
0.3458	1254.27	0.7724	3.021	3.204	3.061	4.4
0.4331	1252.42	0.7553	2.947	3.070	2.926	4.7
0.5070	1250.52	0.7387	2.876	2.957	2.812	4.9
0.6162	1248.49	0.7172	2.785	2.790	2.643	5.3
0.6899	1246.46	0.7041	2.728	2.678	2.529	5.6
0.7811	1245.59	0.6932	2.683	2.538	2.388	5.9
0.8733	1244.62	0.6754	2.611	2.397	2.245	6.3
					APD	5.0

Table 5. Internal pressure of binary liquid mixture (IV) n-decane (x_1) + Cyclohexane (x_2)

x_1	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	% P
0.3563	1248.00	0.7405	2.874	2.965	2.929	1.2
0.3160	1249.50	0.7428	2.888	2.985	2.985	1.6
0.2769	1250.00	0.7442	2.895	3.004	2.949	1.9
0.2677	1252.00	0.7543	2.942	3.008	2.948	2.0
0.2292	1253.50	0.7481	2.923	3.026	2.957	2.3
0.1909	1254.00	0.7500	2.932	2.045	2.965	2.6
0.1638	1255.70	0.7526	2.948	3.058	2.971	2.8
0.1357	1256.00	0.7534	2.952	3.071	2.977	3.1
					APD	2.2

Table 6. Internal pressure of ternary liquid mixture (V) Cyclohexane (x_1) + n-heptane (x_2) + Toluene (x_3)

x_1	X_2	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.1124	0.3962	1328.80	0.7861	3.352	3.078	3.005	2.4
0.1761	0.3766	1319.20	0.7801	3.291	3.074	2.994	2.6
0.2452	0.3379	1317.40	0.7807	3.286	3.086	3.004	2.6
0.3027	0.3032	1307.30	0.7812	3.251	3.098	3.016	2.6
0.3479	0.2837	1321.50	0.7825	3.309	3.100	3.015	2.7
0.3760	0.2894	1318.50	0.7792	3.284	3.085	2.991	3.0
0.3907	0.3050	1323.20	0.7773	3.294	3.066	2.963	3.4
0.4198	0.2416	1308.20	0.7669	3.195	3.114	3.028	2.8
0.4468	0.3796	1321.40	0.7607	3.217	2.978	2.835	4.8
0.4525	0.4393	1303.20	0.7495	3.104	2.021	2.755	5.7
						APD	3.3

Table 7. Internal pressure of ternary liquid mixture (VI) Toluene (x_1) + n-heptane (x_2) + n-hexane (x_3)

x_1	X_2	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.1459	0.2011	1112.10	0.7529	2.458	2.462	2.321	5.7
0.1929	0.2358	1122.00	0.7635	2.526	2.534	2.402	5.2
0.2390	0.2726	1133.80	0.7732	2.599	2.606	2.481	4.8
0.2641	0.2875	1139.90	0.7791	2.640	2.644	2.523	4.6
0.3088	0.3222	1151.50	0.7849	2.700	2.713	2.600	4.2
0.3330	0.3391	1158.00	0.7938	2.754	2.750	2.641	4.0
0.3760	0.3735	1170.30	0.8036	2.832	2.817	2.715	3.6
0.3983	0.3908	1177.20	0.8089	2.876	2.852	2.754	3.5
0.4204	0.3974	1183.00	0.8188	2.933	2.883	2.789	3.2
0.4433	0.4045	1189.00	0.8324	3.005	2.914	2.826	3.0
						APD	4.2

Table 8. Internal pressure of ternary liquid mixture (VII) n-pentane (x_1) + n-hexane (x_2) + Benzene (x_3)

x_1	X_2	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.0966	0.0471	1201.20	0.7432	2.724	3.519	3.341	5.1
0.1428	0.3739	1197.50	0.7416	2.706	2.952	2.748	6.9
0.2017	0.3383	1193.50	0.7361	2.671	2.920	2.692	7.8
0.2590	0.3038	1187.70	0.7286	2.626	2.889	2.637	8.7
0.2984	0.2877	1177.20	0.7281	2.567	2.856	2.587	9.4
0.3075	0.2945	1175.20	0.7175	2.545	2.832	2.559	9.6
0.3420	0.3147	1173.40	0.7073	2.503	2.751	2.463	10.5
0.3685	0.3253	1170.20	0.6953	2.450	2.655	2.354	11.3
0.4099	0.3888	1178.40	0.6838	2.435	2.539	2.220	12.6
0.4082	0.4665	1163.20	0.6688	3.336	2.422	2.103	13.2
						APD	9.5

Table 9. Internal pressure of ternary liquid mixture (VIII) n-Hexane(x_1) + Cyclohexane (x_2) + Benzene (x_3)

x_1	X_2	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.0771	0.4315	1278.10	0.8062	3.243	3.357	3.223	4.0
0.1269	0.4149	1267.50	0.7935	3.152	3.291	3.155	4.1
0.1795	0.3854	1261.20	0.7852	3.096	3.228	3.091	4.2
0.2279	0.3501	1251.20	0.7770	3.027	3.175	3.037	4.3
0.2616	0.3342	1263.50	0.7733	3.058	3.133	2.995	4.4
0.2812	0.3348	1256.30	0.7672	3.008	3.103	2.964	4.5
0.3021	0.3643	1260.20	0.7618	3.000	3.053	2.914	4.6
0.3062	0.3823	1248.40	0.7585	2.945	3.036	2.897	4.6
0.3448	0.4566	1259.10	0.7480	2.942	2.933	2.794	4.8
0.3231	0.4851	1244.20	0.7481	2.890	2.949	2.810	4.7
						APD	4.4

Table 10. Internal pressure of quaternary liquid mixture (IX) n-Pentane (x_1) + Toluene (x_2) + n- Heptane (x_3) + Cyclohexane (x_4)

x_1	X_2	x_3	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.0404	0.6358	0.1544	1270.10	0.8072	3.217	3.231	3.207	0.7
0.0560	0.5737	0.1284	1256.30	0.8026	3.146	3.211	3.170	1.3
0.0735	0.5474	0.1120	1243.50	0.7995	3.086	3.196	3.144	1.6
0.0935	0.5282	0.0959	1230.20	0.7965	3.026	3.182	3.118	2.0
0.1141	0.5054	0.0793	1223.70	0.7927	2.987	3.166	3.090	2.4
0.1134	0.4948	0.0660	1232.30	0.7907	3.012	3.170	3.095	2.4
0.1511	0.4602	0.0487	1218.70	0.7857	2.943	3.136	3.038	3.1
0.1709	0.4395	0.0338	1213.20	0.7840	2.917	3.120	3.011	3.5
0.1071	0.4099	0.0783	1234.50	0.7855	3.000	3.139	3.046	3.0
0.1126	0.4267	0.1137	1218.10	0.7837	2.933	3.120	3.023	3.1
0.1783	0.2174	0.1637	1201.50	0.7498	2.749	2.963	2.782	6.1
0.1991	0.2200	0.1674	1199.20	0.7463	2.728	2.943	2.754	6.4
0.1794	0.6020	0.1451	1233.20	0.7842	2.990	3.104	3.014	2.9
0.1351	0.1100	0.1484	1217.20	0.7492	2.801	2.972	2.788	6.2
0.0948	0.3338	0.2524	1227.50	0.7615	2.883	3.024	2.894	4.4
							APD	3.3

Table 11. Internal pressure of quaternary liquid mixture (X) n-Decane (x_1) + n-Hexane (x_2) + Cyclohexane (x_3) + Benzene (x_4)

x_1	X_2	x_3	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.1171	0.1768	0.1883	1255.30	0.7719	3.022	3.224	3.117	3.3
0.1169	0.1772	0.2769	1255.80	0.7636	2.992	3.171	3.065	3.3
0.1170	0.1769	0.3468	1257.30	0.7553	2.964	3.129	3.024	3.4
0.1245	0.1889	0.4607	1256.00	0.7479	2.931	3.035	2.932	3.4
0.1275	0.3826	0.2080	1251.80	0.7303	2.848	2.886	2.779	3.7
0.1195	0.2478	0.1951	1254.80	0.7558	2.958	3.109	3.002	3.4
0.1158	0.1758	0.1911	1256.40	0.7708	2.022	3.225	3.118	3.3
0.1243	0.1898	0.4087	1254.20	0.7506	2.935	3.065	2.961	3.4
0.1241	0.2570	0.3445	1253.50	0.7431	2.903	3.001	2.895	3.5
0.1253	0.3435	0.2560	1252.30	0.7346	2.866	2.920	2.813	3.7
0.1252	0.4161	0.1828	1254.70	0.7267	2.843	2.850	2.744	3.8
0.2366	0.1992	0.2154	1255.40	0.7476	2.928	3.045	2.970	2.5
0.1749	0.1908	0.2045	1255.70	0.7577	2.968	3.131	3.040	2.9
0.1170	0.1766	0.1894	1258.00	0.7717	3.031	3.224	3.117	3.3
0.0897	0.1727	0.1863	1259.00	0.7768	3.055	3.261	3.147	3.5
							APD	3.4

Table 12. Internal pressure of quaternary liquid mixture (XI) n-Pentane (x_1) + n-Hexane (x_2) + Benzene (x_3) + Toluene (x_4)

x_1	X_2	x_3	u	ρ	P_{int} (theo)	P_{int} (idl)	P_{int} (idl)	%P
0.0943	0.0918	0.4587	1232.10	0.8216	3.235	3.364	3.270	2.8
0.1300	0.1373	0.2974	1233.20	0.8011	3.054	3.223	3.130	2.9
0.1278	0.1288	0.3589	1237.30	0.8054	3.086	3.252	3.148	3.2
0.1450	0.1291	0.3376	1225.70	0.7991	3.019	3.225	2.115	3.4
0.1492	0.1384	0.3421	1217.90	0.7974	2.984	3.209	2.093	3.6
0.1843	0.1484	0.2711	1200.10	0.7855	2.875	3.136	3.011	4.0
0.1823	0.1640	0.3613	1197.90	0.7838	2.861	3.141	2.993	4.7
0.1819	0.1606	0.3842	1200.10	0.7824	2.864	3.152	2.999	4.9
0.1250	0.1665	0.2455	1223.10	0.7975	3.003	3.178	3.094	2.6
0.1691	0.2041	0.2218	1201.30	0.7769	2.848	2.071	2.954	3.8
0.1866	0.0826	0.1250	1229.30	0.7995	3.034	3.180	3.105	2.4
0.1372	0.1580	0.5548	1211.40	0.7926	2.942	3.252	3.090	5.0
0.0660	0.1053	0.7033	1268.10	0.8273	3.289	3.443	3.306	4.0
0.5240	0.1434	0.4201	1260.50	0.8176	3.221	3.340	3.269	2.1
0.1568	0.0468	0.4582	1256.30	0.8184	3.208	3.346	3.221	3.7
							APD	3.5

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