

COMPUTATION OF EXCESS VOLUME, THERMAL EXPANSIVITY AND DENSITY OF TOLUENE+ O- XYLENE AND TOLUENE+ ANILINE USING FLORY'S STATISTICAL THEORY AT ELEVATED PRESSURES

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ABSTRACT

Flory's statistical theory, extended for high pressure, has been applied to compute excess volume, thermal expansivity and density of two binary liquid mixtures in the pressure range 0.1 MPa to 160 MPa at 303.15 K. A good agreement between theoretical and experimental values have been observed confirming the validity of the present approach.

KEYWORDS: Flory's Statistical Theory, Elevated Pressures, Excess Volume, Thermal Expansivity

The deviations from ideal behaviour can best be expressed in terms of excess thermodynamic functions (Rastogi and Mishra, 1995) which give more quantitative idea about the nature of molecular interactions. Excess thermodynamic properties provide information about the molecular interactions and macroscopic behaviour of liquid mixtures, and can be used to test and to improve thermodynamic models for calculating and predicting fluid phase equilibria. Excess molar volume provides a very sensitive test for the molecular solution theory. It reflects not only interactions but also difference between free volumes of the components. Its sign and magnitude give a good estimate of the strength of the unlike interactions in a binary mixture. Extensive work on excess volume of liquid mixtures has been carried out and still in progress by various workers (Van and Patterson, 1982) (Naorem and Suri, 1989) (Singh and Bhatia, 1990).

Thermal expansion coefficient is a very important thermodynamic property and knowledge of this property helps in calculating various thermodynamic parameters. Recently, an empirical relation has been proposed by (Pandey *et al.*, 1997) for computation of thermal expansivity which uses only the values of ultrasonic velocity and density at a given temperature. A number of thermodynamic properties can be evaluated when the sound velocity data are combined with density, pressure and temperature. Ultrasonic velocity, in conjunction with density measurements, permits the direct estimation of adiabatic compressibility and other related parameters which are not easily accessible by any other means.

From the theoretical point of view, excess properties at elevated pressures are of particular interest, as they allow to test the applicability of molecular theories to predict the thermodynamic behaviour of liquids and their mixtures at these conditions. During the

last few years (Oswald *et al.*, 1986) the interest in experimental and theoretical work on thermodynamic properties of liquid mixtures at elevated pressures has greatly increased. In the present work, the values of excess volume, thermal expansion coefficient and density of two binary liquid mixtures have been computed theoretically using Flory's statistical theory at elevated pressures (Pandey and Singh, 2013).

THEORY

The reduced equation of state (Flory, 1965) is given by

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3}-1} - \frac{1}{\bar{V}\bar{T}} \quad (1)$$

This equation has been solved to get expressions for the thermal expansion coefficient (α) and isothermal compressibility (β_T) under the restriction of pressure considerations and also the pressure dependent expressions for the reduced volume (\bar{V}) and reduced pressure (\bar{P}) are derived as

$$\bar{V} = \left[1 + \frac{\alpha T}{3(1-2\beta_T P + \alpha T)} \right]^3 \quad (2)$$

and

$$\bar{P} = \frac{\beta_T P}{(\alpha T - \beta_T P)} \frac{1}{\left[1 + \frac{\alpha T}{3(1-2\beta_T P + \alpha T)} \right]^6} \quad (3)$$

We have calculated reduced volume (\bar{V}) and reduced pressure (\bar{P}) for pure components at elevated pressures using eqs. (2) and (3) with the knowledge of thermal expansion coefficient and isothermal compressibility. Reduced temperature (\bar{T}) has been calculated using these values of \bar{V} and \bar{P} . Characteristic parameters are obtained using their corresponding reduced parameters. The expressions for various thermodynamic properties for binary liquid mixtures have

been derived (Pandey and Singh, 2013) with the help of these parameters, out of which the following eqs. have been used respectively to calculate the values of excess volume (V^E), thermal expansion coefficient (α) and density (ρ) of the binary liquid mixtures under consideration.

The excess volume of the mixture is calculated as

$$V^E = (\sum x_i V_i^*) \tilde{V}^E \tag{4}$$

Thermal expansion coefficient of the mixture has been calculated with the help of pressure-dependent expression given by

$$\alpha = \frac{1}{T} \left[\frac{2\beta\tilde{V}^2}{(\beta\tilde{V}^2+1)} + \frac{1}{3(\tilde{V}^{1/3}-1)} - 1 \right]^{-1} \tag{5}$$

Density is defined as

$$\rho = \frac{M_m}{V} \tag{6}$$

where M_m is the molecular weight of the mixture given by $M_m = \sum X_i M_i$

and M_i is the molecular weight of the i^{th} pure component. The molar volume (V) of the mixture is related with the characteristic volume (V^*) and reduced volume (\tilde{V}) of the mixture as,

$$V = V^* \tilde{V}$$

RESULTS AND DISCUSSION

The values of excess volume, thermal expansivity and density of two binary liquid mixtures have been evaluated with the help of Flory's statistical theory at elevated pressures and at constant temperature of 303.15 K. The two binary mixtures under the present consideration are: toluene+ o-xylene and toluene+ aniline. The desired characteristic and reduced parameters and several other parameters of pure liquid components have been calculated using the method discussed earlier (Pandey and Singh, 2013). Thermal expansivity and isothermal compressibility of pure liquids are evaluated using relations proposed by (Pandey *et al.*, 1997). The density and ultrasonic velocity of pure liquid components and binary mixtures are taken from the literature (Takagi and Teranishi, 1985).

Tables 1 and 2 enlist the computed values of excess volumes of binary mixtures toluene+ o-xylene and toluene+ aniline respectively. Tables 3 and 4 contain the experimental and computed values of thermal expansion coefficient along with the percentage deviations at different concentrations for the respective mixtures. Tables 5 and 6 enlist the experimental and computed values of density along with the percentage deviations at different compositions of toluene+ o-xylene and toluene+ aniline respectively.

A close perusal of table 1 shows that the computed values of excess volume for toluene+ o-xylene are, generally, positive in magnitude with very few exceptions at higher pressure side, indicating weak interactions between component liquids. But in the case of toluene+ aniline (table 2) the values of excess volumes are found to be negative, which show strong interaction between component molecules of the mixture.

Tables 3 and 4 reveal that the computed values of thermal expansion coefficient for both the mixtures toluene+ o-xylene and toluene+ aniline show same trend as experimental one. For both the liquid mixtures, it is clear that as the mole fraction of toluene in the mixture decreases, thermal expansivity decreases over the entire range of pressure. Also, the values of thermal expansion coefficient decrease as the pressure increases at all mole fractions with a very few exceptions in the case of toluene+ aniline. Percentage deviations are less than one for toluene+ o-xylene and less than three percent with some exceptions for toluene+ aniline system.

From tables 5 and 6, it is clear that computed values of density show the same trend as experimental one for both liquid mixtures under the present investigation. For both the liquid mixtures, the tables show that as the mole fraction of toluene in the mixture decreases, the density of the mixtures increases for the entire range of pressure. It is also clear that for each mole fraction, the value of density increases as the pressure increases. The percentage deviations are found to be less than one for toluene+ o-xylene, and for toluene+ aniline it is found to be somewhat greater but maximum value is below ten percent.

Table 1: Calculated values of excess volume of x-toluene + (1-x) o-xylene at 303.15 K

Pressure (MPa)	V^E (cm ³ /mol)			
	x = 0.8	x = 0.6	x = 0.4	x = 0.2
0.1	0.0153	0.0213	0.0211	0.0153
10	0.0096	0.0131	0.0116	0.0056
20	0.0081	0.0108	0.0097	0.0050
30	0.0092	0.0109	0.0095	0.0052
40	0.0076	0.0094	0.0086	0.0054
50	0.0056	0.0075	0.0074	0.0054
60	0.0061	0.0065	0.0052	0.0027
70	-0.0007	0.0004	0.0003	-0.0009
80	0.0030	0.0030	0.0019	0.0002
90	0.0042	0.0041	0.0033	0.0021
100	0.0012	0.0022	0.0026	0.0027
110	-0.0014	-0.0667	-0.0723	-0.0779
120	0.0032	0.0031	0.0028	0.0025
130	-0.0032	-0.0029	-0.0025	-0.0020
140	-0.0017	-0.0007	0.0003	0.0015
150	-0.0036	-0.0039	-0.0040	-0.0040
160	-0.0031	-0.0039	-0.0043	-0.0040

Table 2: Calculated values of excess volume of x-toluene + (1-x) aniline at 303.15 K

Pressure (MPa)	V^E (cm ³ /mol)			
	x = 0.8	x = 0.6	x = 0.4	x = 0.2
0.1	0.0047	0.5078	0.6758	0.8121
10	-0.0186	0.2042	0.2843	0.3623
20	-0.0337	-0.0554	-0.0596	-0.0427
30	-0.0410	-0.0573	-0.0560	-0.0308
40	-0.0473	0.1141	0.1849	0.2689
50	-0.0523	-0.0789	-0.0784	-0.0508
60	-0.0534	0.2355	0.3607	0.4939
70	-0.0630	-0.0926	-0.0973	-0.0753
80	-0.0581	-0.0780	-0.0722	-0.0373
90	-0.0583	0.1936	0.3083	0.4359
100	-0.0625	-0.0938	-0.0968	-0.0719
110	-0.0634	-0.1253	-0.1119	-0.0688
120	-0.0591	-0.0829	-0.0784	-0.0445
130	-0.0658	-0.0950	-0.0932	-0.0619
140	-0.0632	-0.0914	-0.0890	-0.0578
150	-0.0638	-0.0921	-0.0902	-0.0597
160	-0.0629	-0.0919	-0.0905	-0.0604

Table 3: Experimental and calculated values of thermal expansion coefficient of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

$\alpha \times 10^3/(\text{K})$												
Pressure	x = 0.8			x= 0.6			x= 0.4			x = 0.2		
(MPa)	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	1.172	1.171	0.10	1.167	1.166	0.10	1.164	1.161	0.24	1.159	1.156	0.31
10	1.146	1.146	0.00	1.142	1.141	0.08	1.139	1.137	0.22	1.136	1.132	0.32
20	1.124	1.125	-0.07	1.120	1.121	-0.07	1.116	1.116	-0.05	1.112	1.112	-0.04
30	1.105	1.105	0.03	1.101	1.101	-0.05	1.097	1.097	0.00	1.093	1.093	-0.03
40	1.087	1.087	-0.02	1.083	1.083	-0.02	1.079	1.079	0.00	1.075	1.075	0.00
50	1.071	1.071	0.01	1.068	1.067	0.05	1.064	1.064	0.01	1.060	1.060	0.00
60	1.056	1.056	0.02	1.052	1.052	0.07	1.049	1.047	0.14	1.046	1.044	0.25
70	1.043	1.044	-0.03	1.041	1.040	0.09	1.037	1.037	-0.01	1.033	1.033	-0.04
80	1.031	1.031	-0.03	1.028	1.028	0.03	1.025	1.024	0.03	1.021	1.021	-0.02
90	1.019	1.020	-0.04	1.017	1.017	-0.01	1.013	1.014	-0.03	1.011	1.011	0.00
100	1.010	1.010	-0.02	1.007	1.007	-0.05	1.004	1.004	-0.02	1.002	1.002	0.03
110	0.999	0.999	-0.04	0.996	0.997	-0.07	0.994	0.994	0.05	0.992	0.991	0.03
120	0.989	0.990	-0.08	0.987	0.987	-0.05	0.984	0.985	-0.04	0.982	0.982	-0.02
130	0.980	0.981	0.08	0.978	0.979	-0.09	0.976	0.976	-0.06	0.973	0.974	-0.04
140	0.973	0.972	0.02	0.970	0.970	0.01	0.967	0.968	-0.07	0.966	0.966	0.02
150	0.965	0.964	0.05	0.963	0.962	0.03	0.961	0.960	0.04	0.958	0.958	0.01
160	0.957	0.957	0.02	0.955	0.955	0.03	0.953	0.952	0.09	0.951	0.950	0.06

Table 4: Experimental and calculated values of thermal expansion coefficient of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

$\alpha \times 10^3/(\text{K})$												
Pressure	x = 0.8			x= 0.6			x = 0.4			x = 0.2		
(MPa)	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	1.141	1.142	-0.14	1.107	1.140	-2.97	1.068	1.115	-4.37	1.030	1.088	-5.64
10	1.120	1.120	0.06	1.088	1.102	-1.30	1.063	1.074	-2.03	1.017	1.046	-2.83
20	1.101	1.100	0.14	1.070	1.070	0.06	1.038	1.039	-0.13	1.004	1.009	-0.43
30	1.084	1.081	0.19	1.056	1.053	0.23	1.025	1.025	0.01	0.993	0.997	-0.39
40	1.067	1.065	0.12	1.041	1.049	-0.78	1.013	1.027	-1.45	0.983	1.005	-2.17
50	1.052	1.050	0.20	1.028	1.025	0.29	1.001	1.000	0.07	0.974	0.976	-0.19
60	1.038	1.037	0.14	1.016	1.031	-1.44	0.991	1.015	-2.39	0.964	0.998	-3.59
70	1.027	1.025	0.18	1.005	1.002	0.27	0.980	0.979	0.10	0.955	0.957	-0.20
80	1.015	1.013	0.17	0.995	0.991	0.33	0.972	0.970	0.18	0.947	0.949	-0.20
90	1.005	1.002	0.21	0.985	0.997	-1.25	0.964	0.983	-1.97	0.940	0.969	-3.08
100	0.994	0.993	0.13	0.974	0.973	0.19	0.954	0.953	0.19	0.931	0.933	-0.15
110	0.984	0.983	0.13	0.966	0.964	0.23	0.946	0.945	0.13	0.924	0.926	-0.22
120	0.975	0.974	0.11	0.958	0.956	0.21	0.938	0.938	0.07	0.917	0.920	-0.26
130	0.968	0.966	0.20	0.951	0.948	0.23	0.932	0.931	0.10	0.911	0.914	-0.24
140	0.959	0.958	0.14	0.944	0.940	0.34	0.925	0.924	0.17	0.906	0.907	-0.13
150	0.952	0.950	0.22	0.937	0.934	0.32	0.919	0.917	0.19	0.900	0.901	-0.16
160	0.945	0.943	0.15	0.930	0.927	0.29	0.913	0.911	0.15	0.894	0.896	-0.18

Table 5: Experimental and calculated values of density of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

$\rho(\text{gm/cm}^3)$												
Pressure	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
(MPa)	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	0.8605	0.8609	-0.04	0.8605	0.8636	-0.36	0.8605	0.8663	-0.68	0.8605	0.8689	-0.98
10	0.868	0.8684	-0.05	0.8678	0.8711	-0.37	0.8677	0.8736	-0.69	0.8675	0.8761	-0.98
20	0.875	0.8755	-0.06	0.877	0.878	-0.12	0.8796	0.8805	-0.10	0.8822	0.8828	-0.07
30	0.8816	0.8821	-0.06	0.8834	0.8845	-0.13	0.8859	0.8869	-0.11	0.8884	0.8891	-0.08
40	0.8877	0.8883	-0.06	0.8895	0.8906	-0.13	0.8919	0.8929	-0.11	0.8943	0.895	-0.08
50	0.8935	0.8941	-0.07	0.8952	0.8964	-0.13	0.8976	0.8985	-0.12	0.8999	0.9006	-0.08
60	0.899	0.8996	-0.07	0.9006	0.9018	-0.13	0.9028	0.9039	-0.12	0.9052	0.9059	-0.08
70	0.9042	0.9048	-0.07	0.9058	0.9069	-0.13	0.9079	0.909	-0.12	0.9102	0.911	-0.09
80	0.9091	0.9097	-0.07	0.9107	0.9118	-0.13	0.9127	0.9139	-0.12	0.915	0.9158	-0.09
90	0.9138	0.9144	-0.07	0.9154	0.9165	-0.13	0.9174	0.9185	-0.13	0.9196	0.9204	-0.09
100	0.9164	0.919	-0.07	0.9199	0.921	-0.12	0.9218	0.923	-0.13	0.924	0.9248	-0.09
110	0.9227	0.9233	-0.06	0.9242	0.9253	-0.12	0.9261	0.9272	-0.13	0.9282	0.9291	-0.09
120	0.9269	0.9275	-0.06	0.9283	0.9295	-0.12	0.9302	0.9314	-0.13	0.9323	0.9332	-0.09
130	0.9309	0.9315	-0.06	0.9323	0.9334	-0.12	0.9341	0.9353	-0.13	0.9363	0.9371	-0.09
140	0.9348	0.9353	-0.06	0.9362	0.9373	-0.12	0.938	0.9392	-0.13	0.9401	0.9409	-0.09
150	0.9385	0.9391	-0.06	0.9399	0.941	-0.11	0.9417	0.9429	-0.13	0.9437	0.9446	-0.09
160	0.9422	0.9427	-0.06	0.9436	0.9446	-0.11	0.9453	0.9465	-0.13	0.9473	0.9482	-0.09

Table 6: Experimental and calculated values of density of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

$\rho(\text{gm/cm}^3)$												
Pressure	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
(MPa)	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	0.8854	0.9061	-2.34	0.9136	0.952	-4.21	0.9462	1.0032	-6.02	0.9789	1.0573	-8.01
10	0.8924	0.9137	-2.40	0.9198	0.9619	-4.57	0.9518	1.0137	-6.50	0.9841	1.0681	-8.53
20	0.8989	0.9208	-2.44	0.9258	0.971	-4.88	0.9572	1.0234	-6.92	0.9892	1.0783	-9.01
30	0.9051	0.9274	-2.46	0.9314	0.9773	-4.93	0.9624	1.0294	-6.97	0.9941	1.0838	-9.03
40	0.911	0.9336	-2.48	0.9368	0.9815	-4.77	0.9673	1.0324	-6.72	0.9988	1.0855	-8.68
50	0.9165	0.9394	-2.49	0.9419	0.9889	-4.99	0.9721	1.0405	-7.04	1.0033	1.0942	-9.06
60	0.9218	0.9448	-2.50	0.9468	0.9911	4.67	0.9767	1.0408	-6.57	1.0077	1.0927	-8.43
70	0.9268	0.95	-2.51	0.9515	0.9994	-5.03	0.981	1.0506	-7.09	1.012	1.1039	-9.08
80	0.9316	0.955	-2.51	0.9561	1.0042	-5.04	0.9853	1.0553	-7.10	1.0161	1.1082	-9.07
90	0.9362	0.9597	-2.51	0.9604	1.0059	-4.74	0.9894	1.0554	-6.67	1.0201	1.1067	-8.50
100	0.9406	0.9642	-2.51	0.9646	1.0134	-5.05	0.9934	1.0643	-7.14	1.024	1.117	-9.09
110	0.9449	0.9686	-2.51	0.9687	1.0176	-5.06	0.9972	1.0684	-7.14	1.0277	1.1209	-9.07
120	0.949	0.9728	-2.50	0.9726	1.0218	-5.06	1.001	1.0725	-7.14	1.0314	1.1249	-9.06
130	0.953	0.9768	-2.50	0.9764	1.0258	-5.06	1.0046	1.0764	7.15	1.035	1.1288	-9.06
140	0.9588	0.9807	-2.49	0.9801	1.0296	-5.06	1.0081	1.0802	-7.15	1.0385	1.1325	-9.06
150	0.9606	0.9844	-2.49	0.9836	1.0334	-5.06	1.0116	1.084	-7.16	1.0419	1.1362	-9.05
160	0.9642	0.9881	-2.48	0.9871	1.0371	-5.06	1.0149	1.0876	-7.16	1.0452	1.1398	-9.05

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