Int J Thermophys (2008) 29:1376–1384
DOI 10.1007/s10765-008-0444-7

Thermophysical Properties of Binary Mixtures of Methanol with Chlorobenzene and Bromobenzene from 293 K to 313 K

Divya Shukla · Shashi Singh · Shahla Parveen ·
Manisha Gupta · J. P. Shukla

Received: 8 December 2006 / Accepted: 25 April 2008 / Published online: 18 June 2008

Abstract Densities and viscosities have been measured for the binary mixtures of methanol with chlorobenzene and with bromobenzene from 293 K to 313 K over the complete composition range. Densities were used to compute the excess molar volume ($V_{\mathrm{m}}^{\mathrm{E}}$), for these binary systems. The results have been discussed in terms of molecular interactions. Furthermore, viscosity results were compared with a corresponding-states model. The average absolute deviation was found to be 1.9 %.

Keywords Binary mixture · Bromobenzene · Chlorobenzene · Density · Intermolecular interaction · Methanol · Viscosity

1 Introduction

Scientists and engineers often require the physical and chemical properties of gases and liquids for technological process design. The chemical or process engineer, in particular, finds knowledge of physical properties of fluids essential for designing many kinds of industrial equipment. The physical properties of every substance depend directly on the nature of the molecules of the substances. The estimation of physical properties would provide reliable physical and thermodynamic properties for the pure substances and for mixtures at any temperature and composition, which provide useful information about molecular structure and intermolecular forces in liquid mixtures [1–3]. Ali et al. [4] have discussed excess properties in terms of molecular interactions in binary mixtures of N-N dimethylacetamide with alcohol, toluene, and chlorobenzene.

D. Shukla · S. Singh · S. Parveen · M. Gupta (✉) · J. P. Shukla
Department of Physics, University of Lucknow, Lucknow, Uttar Pradesh 226007, India
e-mail: guptagm@rediffmail.com

The viscosity of binary mixtures provides information on the structure of individual liquid components in industrial processes that involve mass transfer, fluid flow, and viscosity build-up. Also, the well-recognized importance of thermodynamic and thermophysical properties in design calculations, involving chemical separation and heat transfer, has motivated us to carry out systematic measurements of various acoustic and thermodynamic properties of binary mixtures. Continuing with our studies, we focus here on volumetric and viscometric studies of binary mixtures of methanol with chlorobenzene and bromobenzene.

Methanol forms the basis for many products including silicon refrigerants, adhesives, etc., and it may also be used as a fuel source in fuel cells. Aryl halides (chlorobenzene, bromobenzene) having a special kind of structure, nucleophilic substitution proceeds readily and can be used for synthetic purposes. In the present study, we have carried out density and viscosity measurements of binary mixtures of methanol with chlorobenzene and bromobenzene over the complete composition range at temperatures of (293, 303, and 313) K. Using the experimental data, excess molar volumes (V_m^E) have been evaluated and results have been discussed in terms of molecular association between unlike molecules. Experimental viscosities were also compared with a corresponding-states model. Good agreement has been found between the experimental and theoretically evaluated viscosities.

2 Experimental

Mixtures were prepared by weighing the liquids in specially designed ground glass stoppered bottles, taking extreme precautions to minimize preferential evaporation. A Sartorius (BP 121S) single-pan balance having a stated precision of 0.1 mg was used. The maximum possible error in the mole fraction is estimated to be ±0.0001. The density has been measured with an uncertainty of $\pm 0.0005\ \mathrm{g \cdot cm^{-3}}$ using a single capillary pyknometer. For each solution, 4–5 density measurements were taken and the results were averaged.

All measurements have been determined at three temperatures, (293, 303, and 313) K, using a microprocessor-based temperature controller (Julabo F25 HD) (uncertainty of ±0.01 °C).

The viscosity of the mixtures was determined using Ostwald's viscometer, which was located inside a double-walled jacket. For each solution, the experimental viscosity was obtained by averaging 5–6 flow-time measurements. The uncertainty in the viscosity measurements was within ±0.5 %.

The chemicals used were obtained from Ranbaxy Fine Chemicals Limited. All the chemicals used were purified by standard procedures, discussed by Perrin and Armarego [6]. The purities of all the chemicals were ascertained by the constancy of their boiling points during final distillation, and also by literature comparisons [5–10] of their densities and viscosities at (293, 303, and 313) K as shown in Table 1. These values agreed within experimental error.

Table 1 Comparisons of measured boiling points, densities (ρ), and viscosities (η) of pure liquids with literature values at selected temperatures

Liquids	Temp (K)	Boiling point (T_b)		$\rho\,(\mathrm{g \cdot cm^{-3}})$		$\eta\,(\mathrm{mPa \cdot s})$	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Methanol	293	64.1	64.6[a]	0.7911	0.7914[a] 0.7915[b] 0.7914[e]	0.5910	0.5910[b]
	303			0.7819	0.7820[b] 0.7820[e]	0.5180	0.5140[b]
	313			0.7724	0.7726[b] 0.7724[e]	0.4500	0.4480[b]
Chlorobenzene	293	131.7	131.1[a]	1.1058	1.1058[a] 1.1064[e]		
	303			1.0950	1.0950[c] 1.0956[d]	0.7210	0.7250[c]
	313			1.0852	1.0848[e]		
Bromobenzene	293	156.0	156.5[a]	1.4970	1.4950[a]		
	303			1.4830	1.4810[c] 1.4814[d]	0.9844	1.013[c]
	313			1.4680	1.4680[d]		

[a] Ref. [5]
[b] Ref. [7]
[c] Ref. [8]
[d] Ref. [9]
[e] Ref. [10]

3 Results and Discussion

Table 1 gives the comparisons of measured values of boiling point, densities (ρ) and viscosities (η) of pure liquids with corresponding literature values at (293, 303, and 313) K. Tables 2 and 3 list the experimental values of densities (ρ) and viscosities (η) of binary mixtures of methanol with chlorobenzene and bromobenzene at (293, 303, and 313) K.

The densities measured over the entire composition range of binary mixtures were used for calculating the excess molar volume V_m^E, using the relation,

$$V_\mathrm{m}^\mathrm{E} = V_\mathrm{m} - \sum_{i=1}^{2} x_i V_i \tag{1}$$

where V_m is the molar volume of the mixture, and V_i and x_i are the molar volume and mole fraction of pure component i ($i = 1, 2$).

The values of V_m^E are plotted against the mole fraction of methanol in Fig. 1.

Table 2 Densities (ρ) and viscosities (η) for methanol (1) + chlorobenzene (2) mixtures at (293, 303, and 313) K

x_1	$\rho\,(\mathrm{g \cdot cm^{-3}})$	$\eta\,(\mathrm{mPa \cdot s})$
$T = 293\,\mathrm{K}$		
0.0000	1.1058	0.8432
0.2808	1.0665	0.8312
0.4676	1.0292	0.8209
0.6010	0.9939	0.8018
0.7009	0.9605	0.7699
0.7783	0.9288	0.7256
0.8405	0.8985	0.6920
0.8913	0.8697	0.6766
0.9335	0.8423	0.6424
0.9693	0.8162	0.6194
1.0000	0.7911	0.5910
$T = 303\,\mathrm{K}$		
0.0000	1.0950	0.7210
0.2808	1.0560	0.7121
0.4676	1.0190	0.6924
0.6010	0.9837	0.6821
0.7009	0.9504	0.6572
0.7783	0.9189	0.6093
0.8405	0.8888	0.5828
0.8913	0.8601	0.5672
0.9335	0.8329	0.5401
0.9693	0.8068	0.5280
1.0000	0.7819	0.5180
$T = 313\,\mathrm{K}$		
0.0000	1.0820	0.6247
0.2808	1.0440	0.6157
0.4676	1.0070	0.6041
0.6010	0.9725	0.5832
0.7009	0.9394	0.5569
0.7783	0.9081	0.5296
0.8405	0.8783	0.5100
0.8913	0.8499	0.4961
0.9335	0.8229	0.4701
0.9693	0.7971	0.4591
1.0000	0.7724	0.4500

Table 3 Densities (ρ) and viscosities (η) for methanol (1) + bromobenzene (2) mixtures at (293, 303, and 313) K

x_1	$\rho\,(\mathrm{g \cdot cm^{-3}})$	$\eta\,(\mathrm{mPa \cdot s})$
$T = 293\,\mathrm{K}$		
0.0000	1.4970	1.164
0.3528	1.3810	1.124
0.5504	1.2800	1.008
0.6775	1.1920	0.8873
0.7657	1.1140	0.8144
0.8305	1.0450	0.7619
0.8802	0.9830	0.7235
0.9195	0.9276	0.6860
0.9552	0.8714	0.6570
0.9778	0.8323	0.6312
1.0000	0.7911	0.5910
$T = 303\,\mathrm{K}$		
0.0000	1.4830	0.9844
0.3528	1.3670	0.9306
0.5504	1.2670	0.8356
0.6775	1.1790	0.7420
0.7657	1.1020	0.6962
0.8305	1.0330	0.6467
0.8802	0.9721	0.6170
0.9195	0.9172	0.5891
0.9552	0.8615	0.5651
0.9778	0.8228	0.5344
1.0000	0.7819	0.5180
$T = 313\,\mathrm{K}$		
0.0000	1.4670	0.8786
0.3528	1.3520	0.8142
0.5504	1.2530	0.7399
0.6775	1.1660	0.6444
0.7657	1.0890	0.6019
0.8305	1.0210	0.5686
0.8802	0.9607	0.5451
0.9195	0.9064	0.5130
0.9552	0.8511	0.4900
0.9778	0.8129	0.4773
1.0000	0.7724	0.4500

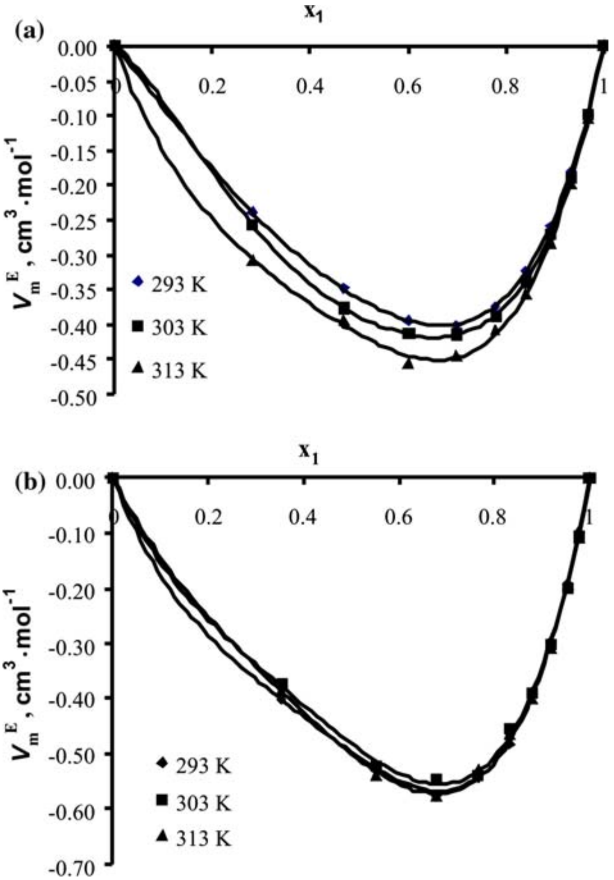

Fig. 1 (**a**) Excess molar volume versus mole fraction of methanol for methanol (1) + chlorobenzene (2) mixtures at varying temperatures and (**b**) excess molar volume versus mole fraction of methanol for methanol (1) + bromobenzene (2) mixtures at varying temperatures

The values of the excess molar volume of the binary mixtures of methanol with chlorobenzene and bromobenzene may be interpreted as the results of the contribution of the various types of intermolecular interactions operating between the components of these mixtures: (i) physical, due to non-specific Van der Waals type interactions; (ii) chemical, due to hydrogen bonding; and (iii) structural, due to changes of interstitial accommodation and free volume. Each factor makes positive or negative contributions to the resultant values of excess molar volume, and the magnitude of the contribution is dependent on the mole fraction range.

Figure 1a, b displays the behavior of the excess molar volume for both systems. Values of V_m^E show negative deviations over the entire composition range, with minima at around $x_1 = 0.6$–0.7 for both systems. The observed values of V_m^E in both mixtures could be attributed to chemical transfer forces, formation of hydrogen bonding, and other complex forming interaction-making negative contributions. Methanol is a liquid of self-associative type in the pure state and exhibits an equilibrium between multimer

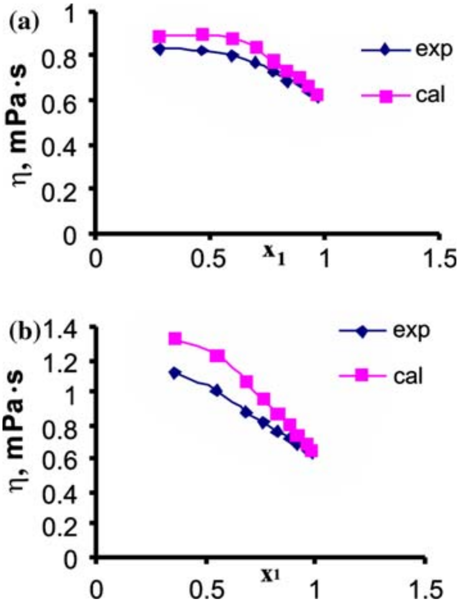

Fig. 2 (**a**) Comparison of experimental and calculated viscosities for methanol (1) + chlorobenzene (2) mixtures at 293 K and (**b**) comparison of experimental and calculated viscosities for methanol (1) + bromobenzene (2) mixtures at 293 K

and monomer species. In the pure state, halogenated compounds exhibit weak dipole–dipole interactions. When chlorobenzene/bromobenzene is mixed with methanol, the halogenated solvent can interact with the –OH group and this can lead to formation of intermolecular complexes through dipole–dipole interactions. The molar volumes of methanol, chlorobenzene, and bromobenzene at 293 K are (40.50, 101.79, and 104.88) $\text{cm}^3 \cdot \text{mol}^{-1}$, respectively. A larger molar volume difference between methanol and bromobenzene/chlorobenzene would allow a more favorable packing of chlorobenzene/bromobenzene molecules into the spaces created by methanol molecules. This would result in a contraction in volume; and hence would give rise to negative values of the excess molar volume. Thus, it seems that the packing effect, as well as the formation of hydrogen bonds, are the determining factors for interactions in these mixtures.

Negative values of the excess molar volume have been reported by Orge et al. [11] and Serbanovic et al. [10] for binary mixtures of methanol with chlorobenzene. Our results of V_m^E show good agreement with the results reported by Orge et al. [11] and Serbanovic et al. [10]. Nayak et al. [8] and Rathnam et al. [9] have also reported similar variations in V_m^E for the binary mixtures of ethyl chloroacetate with chlorobenzene and methyl formate with chlorobenzene and bromobenzene. The effect of temperature on values for both mixtures is insignificant.

4 Modeling

Mixture viscosities were predicted using a recently proposed corresponding-states model [12,13]. This model is based on pure-component properties: critical temperature T_C, critical volume V_C, and the viscosity of the three chosen fluids: methanol, chlorobenzene, and bromobenzene at (293, 303, and 313) K (Fig. 2).

$$\varphi = \frac{V_c^{2/3}}{(MT_c)^{1/2}} \tag{2}$$

$$\ln(\eta_m \varphi_m) = x_i \ln(\eta_i \varphi_i) + x_j \ln\left(\eta_j \varphi_j\right) \tag{3}$$

where the symbols have their usual meanings.

Reference fluid data were correlated as a function of temperature according to

$$\ln \eta = A + \frac{B}{T} \tag{4}$$

where A and B are adjustable parameters. These are presented in Table 4, together with the required critical properties.

Mixing and combining rules are described below:

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{5}$$

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{6}$$

$$V_{cij} = \frac{1}{8}(V_{ci}^{1/3} + V_{cj}^{1/3})^3 \tag{7}$$

$$T_{cij} = \sqrt{T_{ci} T_{cj}} \frac{\sqrt{V_{ci} V_{cj}}}{V_{cij}}^{(n/3-1)} \tag{8}$$

where x is the mole fraction, indices i and j represent pure components, and m represents the mixture property. In the above calculations, the parameter n was set equal to 4.6. The results show that by using only pure-component data of each

Table 4 Critical parameters and constants of reference fluid

Reference fluid	T_c (K)	V_c (cm$^3 \cdot$ mol^{-1})	A	B
Methanol	512.60	118	1248.9	−4.7857
Chlorobenzene	632.40	308	1375.5	−4.8656
Bromobenzene	670	324	1289.6	−4.2487

reference fluid, one is able to estimate all of the corresponding mixture data points with relatively small deviations. Good agreement has been found between the experimental viscosities and those calculated using the corresponding-states model. An average absolute deviation of 1.9 % was found for the 54 mixture data points measured in this work.

5 Conclusion

The observed negative values of the excess molar volume indicate the presence of strong dipole–dipole interactions. Viscosities of mixtures were correlated with a new corresponding-states model. An average absolute deviation of less than 2 % demonstrates the reliability of this model to estimate the viscosity of these systems.

References

1. N.N. Wankhede, M.K. Lande, B.R. Arbad, J. Chem. Eng. Data. **50**, 969 (2005)
2. B. Gonzalez, A. Dominguez, J. Tojo, J. Chem. Thermodyn. **36**, 267 (2004)
3. A. Ali, Abida, S. Hyder, A.K. Nain, Int. J. Phys. **5**, 661 (2002)
4. A. Ali, A.K. Nain, Pramana-J. Phys. **58**, 695 (2002)
5. D.R. Lide, *CRC Handbook of Chemistry and Physics*, 76th edn., sect. 14 (CRC Press, Boca Raton, 1996), p. 34
6. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*. (Pergamon Press, Oxford, 1988)
7. C.-H. Tu, C.-Y. Liu, W.-F. Wang, Y.-T. Chou, J. Chem. Eng. Data. **45**, 450 (2000)
8. J.N. Nayak, M.I. Aralaguppi, T.M. Aminabhavi, J. Chem. Eng. Data. **48**, 628 (2003)
9. M.V. Rathnam, R.K.R. Singh, J. Chem. Eng. Data. **53**, 265 (2008)
10. S.P. Serbanovic, M.L. Kijevcanin, I.R. Radovic, B.D. Djordjevic, Fluid Phase Equilib. **239**, 69 (2006)
11. B. Orge, M. Iglesias, J. Tojo, J.L. Legido, J. Chem. Thermodyn. **6**, 121 (1994)
12. A.S. Teja, P. Rice, Ind. Eng. Chem. Fundam. **20**, 77 (1981)
13. G. Scalabrin, G. Cristofoli, M. Grigiante, Int. J. Thermophys. **26**, 429 (2005)