J. Indian Inst. Sci., 66, July 1986, pp. 449–456

Thermophysical properties of alkylbenzene-chloroethane systems – viscosity and surface tension

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Received on November 22, 1984; Revised on July 22, 1986.

Abstract

Experimental measurements on the viscosity and surface tension of some binary mixtures formed by one component each from the first three members of the alkylbenzenes (benzene, toluene, and *p*-xylene) and the three chloroethanes (1,2-dichloro, 1,1,1-trichloro- and 1,1,2,2-tetrachloro-) are reported as a function of temperature. The results are analysed for their predictability and generality.

Key words: Viscosity, surface tension, alkylbenzenes, chloroethanes, benzene, toluene, *p*-xylene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, mixtures, thermophysical properties.

1. Introduction

Alkylbenzenes (such as benzene, toluene, *p*-xylene) and chloroethanes (such as 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane) are important as raw materials, solvents, cleaning agents, etc., in several industrial operations. Data on the thermophysical properties of these compounds, as well as those on the binary mixtures (formed from one compound of each of the two series), can provide us with a host of valuable information of general nature such as: (a) effect of alkyl substitution on the benzene ring, (b) effect of successive chlorination on the chloroethanes, (c) effect of different types of interactions between the molecules, and (d) the effect of temperature and composition. The dependability and value of the general conclusions are enhanced if they are based on careful observations from a single laboratory, where experiments are conducted under conditions which ensure equally good measurement for all the substances and systems chosen for the study, rather than on the fragmented data from the literature. Hence, a programme to evaluate the thermophysical properties of the alkylbenzene-chloroethane systems is undertaken in our laboratories.

2. Purity of the samples

The pure liquids used in the present work are prepared from the AnalaR/guaranteed reagent grade, further purified according to the methods described by Weissberger[1] and Reddick and Bunger[2]. Based on the closeness of the agreement of the physical property data given in Table I, with selected values from the literature[3-5], and on the accuracy of the calibration charts and tables prepared and used to check the composition of the mixtures used in the present experiments: (a) the pure liquids are estimated to be of purity better than 99.5% and (b) the composition of the mixtures reported are within ±0.01 mole per cent of their true values.

3. Experimental methods

Among the various methods available for the measurement of viscosity and surface tension, those described below have been chosen keeping in view: (a) simplicity and ease of operation, (b) suitability for the ranges of temperature and the set of systems chosen for the study and (c) ease of fabrication/standardization/testing, etc.

A Hoppler viscometer, with provision to maintain the temperature of the test liquid to within ± 0.05°C of the desired set point, is used to determine the viscosity of the liquids and liquid mixtures. The measurements on the fall times of the ball are accurate to within ± 0.05 sec. Comparison of the pure liquid data with evaluated data from the literature[6] showed that the viscosities reported in this work are within ± 2%. A detailed description of the experimental work as well as a bibliography of references on the topic are given by Prabhakar[7]. Experiments are conducted in the temperature range 25–70°C and on the mixtures of three alkylbenzenes with 1,2-dichloroethane and 1,1,1-trichloroethane.

Table I
Comparison of refractive index and density of the pure liquids used in the present study with selected values from the literature at 30 + 0.05°C

Substance	Density, g/ml		Refractive index	
	Present work	Literature	Present work	Literature
Benzene	0.8682	0.8681	1.4945	1.4946
Toluene	0.8575	0.8576	1.4914	1.4913
p-Xylene	0.8525	0.8524	1.4905	1.4904
1,2-Dichloroethane	1.2391	1.2390	1.4392	1.4392
1,1,1-Trichloroethane	1.3210	1.3209	1.4321	1.4320
1,1,2,2-Tetrachloroethane	1.5785	1.5786	1.4883	1.4884

A tensiometer operating on the general principles outlined by Catchpole and Ellis[8] and described in detail by Ashok Kumar[9] is used in the present study. The method involves the measurement of the maximum pressure differential developed by a dry gas when the bubble detaches from: (a) uniform capillary of about 1 mm bore and (b) a very fine capillary, both immersed to the same depth into the test liquid maintained at the desired temperature to within ± 0.05°C. Comparison of the pure liquid data with the selected values of Jasper[10] showed that the present measurements are accurate to within ±0.35%. Experiments are conducted in the temperature range 20–80°C, on the binary mixtures formed by *p*-xylene with the three chloroethanes and 1,1,1-trichloroethane with benzene and toluene.

Measurements on density, necessary input to methods, described above for viscosity and surface tension are carried out by means of carefully calibrated pyknometers. The weights required in the work are taken in a mettler balance accurate to 0.0001 g and the temperatures desired are maintained within ± 0.05°C. Pure liquid data agreed with literature values[3-5] to within ± 0.05%.

4. Results and discussion

The experimental data on viscosity and surface tension of the substances and mixtures studied in the present work are given in Tables II-V. The density data on all the systems studied could be predicted using the law of additive volumes rewritten for convenience as:

$$\rho_m = \frac{\rho_1 \ \rho_1}{\rho_2 x_1 + \rho_1 x_2} \tag{1}$$

with a per cent average absolute deviation of 1.7% (from their pure component values). The data are not tabulated in this paper in view of simplicity of the experimentation.

Viscosity data on the six binary mixtures given in Table III have been compared with the values predicted from Arrhenius equation·

Table II
Viscosity of pure liquids

Substance	Viscosity in Cp at temperature in °C			
	25	40	55	70
Benzene	0.7085	0.5342	0.4431	0.3560
Toluene	0.5708	0.4610	0.4195	0.3710
p-Xylene	0.6077	0.5020	0.4345	0.3880
1,2-Dichloroethane	0.7810	0.6263	0.5773	0.4657
1,1,1-Trichloroethane	0.6762	0.5875	0.5140	0.4400

Table III
Viscosity of alkyl benzene-chloroethane systems

Temperature 25°C		40°C		55°C		70°C	
x_1	η	x_1	η	x_1	η	x_1	η
1,2-Dichloroethane-benzene system							
0.808	0.7340	0.819	0.6192	0.802	0.5245	0.807	0.4505
0.620	0.6947	0.628	0.5439	0.609	0.4846	0.619	0.4166
0.414	0.6770	0.429	0.5130	0.400	0.4383	0.406	0.4023
0.202	0.6849	0.219	0.5175	0.199	0.4322	0.198	0.3895
1,2-Dichloroethane-toluene system							
0.849	0.7240	0.839	0.5906	0.849	0.5286	0.839	0.4359
0.653	0.6470	0.632	0.5310	0.653	0.4699	0.632	0.3691
0.465	0.6080	0.455	0.4970	0.465	0.4437	0.455	0.3851
0.245	0.5783	0.250	0.4804	0.245	0.4325	0.250	0.3777
1,2-Dichloroethane-p-xylene system							
0.867	0.7234	0.842	0.5365	0.867	0.5024	0.867	0.4399
0.705	0.6569	0.660	0.5059	0.705	0.4825	0.705	0.4207
0.514	0.6323	0.461	0.4930	0.514	0.4562	0.514	0.4017
0.290	0.6147	0.255	0.4942	0.290	0.4408	0.290	0.3953
1,1,1-Trichloroethane-benzene system							
0.798	0.6530	0.783	0.5452	0.785	0.4664	0.785	0.4370
0.564	0.6424	0.593	0.5175	0.593	0.4455	0.593	0.4085
0.371	0.6452	0.396	0.5205	0.396	0.4203	0.396	0.4096
0.162	0.6419	0.200	0.4799	0.180	0.4087	0.180	0.3796
1,1,1-Trichloroethane-toluene system							
0.805	0.6751	0.805	0.5654	0.805	0.4989	0.805	0.4325
0.619	0.6711	0.619	0.5579	0.619	0.4766	0.619	0.4311
0.389	0.6394	0.389	0.5059	0.389	0.4498	0.389	0.4044
0.212	0.5785	0.212	0.4772	0.212	0.4127	0.212	0.3781
1,1,1-Trichloroethane-p-xylene system							
0.778	0.6399	0.828	0.5645	0.828	0.4736	0.778	0.4079
0.595	0.6198	0.649	0.5455	0.649	0.4605	0.595	0.4004
0.386	0.6044	0.444	0.5169	0.324	0.4411	0.386	0.3923
0.193	0.5726	0.224	0.5098	0.224	0.4337	0.193	0.3815

$$ln\ \eta_m = x_1\ ln\ \eta_1 + x_2\ ln\ \eta_2$$

and Lobe's equation:

$$\left(\frac{\eta}{\rho}\right)_m = \phi_1\left(\frac{\eta_1}{\rho_1}\right)e^{\phi_2\alpha_2} + \phi_2\left(\frac{\eta_2}{\rho_2}\right)e^{\phi_1\alpha_1} \qquad (2)$$

where

$$\alpha_1 = -1.7 \ln \frac{(\eta_1/\rho_1)}{(\eta_2/\rho_2)} \tag{3}$$

and

$$\alpha_2 = 0.27 \ln \frac{(\eta_2/\rho_2)}{(\eta_1/\rho_1)} + \left[1.3 \ln \frac{(\eta_2/\rho_2)}{(\eta_1/\rho_1)}\right]^{0.5}. \tag{4}$$

They have also been compared with the rheochor method

$$n_m^{1/8} = \left(\frac{x_1 Rh_1 + x_2 Rh_2}{M_1 x_1 + M_2 x_2} \right) \rho_m . \tag{5}$$

The per cent average absolute deviations on an overall basis are: 4.6 for Arrhenius method, 8.8 for Lobe's method and 22.5 for the rheochor method. It is noteworthy that pure liquid viscosity data of this set of compounds are predicted by the rheochor method with a per cent average absolute deviation of 17.6. It is therefore suggested that the liquid mixture viscosity data of similar systems be estimated using Arrhenius equation in preference to the other methods

The pure liquid surface tension data given in Table IV and the mixture data given in Table V are compared with the predictions from Brock and Bird[11] method:

$$\gamma = P_c^{2/3}\ T_c^{1/3}\ (0.133\ \alpha_c\ - 0.281)\,(1 - T_R)^{11/9} \tag{6}$$

Table IV
Surface tension of pure liquids

Temp. °C	γ dyne/cm	Temp. °C	γ dyne/cm	Temp. °C	γ dyne/cm
Benzene		*Toluene*		*p*-Xylene	
20	28.80	20	28.40	20	28.50
28	27.82	30	27.34	40	26.22
48	25.32	50	25.13	66	23.49
68	22.82	70	22.91	80	22.00
		80	21.30		
1,2-Dichloroethane		*1,1,1-Trichloroethane*		*1,1,2,2-Tetrachloroethane*	
36	30.41	28	24.80	22	35.97
52	28.12	51	21.95	36	34.12
60	26.80	60	20.75	52	32.46
74	25.36	69	19.53	61	31.13
				75	29.33

Table V
Surface tension of alkylbenzene-chloroethane systems

x_1	t	γ	t	γ	t	γ	t	γ
Benzene-1,1,1-trichloroethane system								
0.3653	24.3	25.93	40.5	24.96	60.0	21.36	77.8	18.45
0.6376	21.5	26.79	41.2	24.37	60.0	22.34	78.3	20.32
0.8270	24.0	26.39	41.4	25.02	60.5	22.69	79.0	20.75
Toluene-1,1,1-trichloroethane system								
0.3324	19.5	25.53	40.0	23.74	60.3	21.53	75.5	19.38
0.6037	19.4	27.47	40.6	24.89	60.5	22.71	80.5	20.35
0.8036	22.0	27.76	40.5	25.09	60.5	23.17	80.0	21.66
p-Xylene-1,1,1-trichloroethane system								
0.3136	18.7	26.10	41.0	22.99	50.0	21.98	60.5	21.10
0.3136	70.0	21.14	78.5	19.16	—	—	—	—
0.5474	20.0	26.13	40.0	26.22	60.5	22.03	70.0	20.56
0.5474	80.5	19.30	—	—	—	—	—	—
0.7884	20.0	24.84	40.5	23.00	60.5	21.54	69.5	21.42
0.7884	79.5	20.78	—	—	—	—	—	—
p-Xylene-1,2-dichloroethane system								
0.2625	20.0	26.22	40.5	25.25	50.5	24.75	60.5	22.62
0.2625	71.0	20.98	80.0	20.10	—	—	—	—
0.4810	21.0	27.56	40.0	23.20	50.5	22.62	60.5	22.05
0.4810	70.5	21.43	80.0	20.80	—	—	—	—
0.7338	19.8	27.89	40.8	25.69	50.0	24.75	60.8	22.14
0.7338	71.0	21.79	78.5	21.13	—	—	—	—
p-Xylene-1,1,2,2-tetrachloroethane system								
0.3515	19.5	31.27	40.8	28.30	50.5	26.86	60.0	25.48
0.3515	80.0	23.86	—	—	—	—	—	—
0.6284	20.0	28.87	39.5	25.79	60.5	24.58	70.5	23.26
0.6284	80.6	21.81	—	—	—	—	—	—
0.8318	22.5	26.69	41.0	25.58	61.0	23.38	70.5	21.37
0.8318	80.3	20.50	—	—	—	—	—	—

and Prasad's[12] method

$$\gamma = [0.4 + 0.009R_M + 0.00108\,(4\pi N\mu^2/9\,k\,T_c)\,P_c^{2/3}\,T_c^{1/3}\,(1-T_R)^{11/9}] \quad (7)$$

and values from the linear rule in mole fraction

$$\gamma_m = \gamma_1 x_1 + \gamma_2 x_2. \quad (8)$$

On an overall basis the per cent average absolute deviations are: 8.1 for Brock and Bird method, 7.2 for Prasad's method and 5.4 for the linear rule in mole fraction. It is, therefore, recommended that the surface tension of similar systems be estimated from the linear rule in mole fractions in preference to the other methods. Investigations on the other thermophysical properties of the alkylbenzene-chloroethane systems and some other characteristic systems are in progress.

Nomenclature

k : Boltzmann's constant
M : Molecular weight
P : Pressure, atm.
t : Temperature, °C
T : Temperature, °K
Rh : Rheochor
R_M : Molar refraction, cc/g mole
x : Mole fraction

Greek

α : Constant defined by equations (3) and (4)
α_c : Riedel parameter
γ : Surface tension, dyne/cm
ρ : Density, g/cc
μ : Dipole moment, debyes
η : Viscosity centipoise
ϕ : Volume fraction

Subscripts

1 : Component 1
2 : Component 2
C : Critical point
m : Mixture
R : Reduced

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