

Viscosities of binary mixtures containing one polar component

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Abstract. Viscosities of binary mixtures, benzene + benzonitrile, benzene + methylpropylketone and cyclohexane + methylpropylketone were determined at 303.15 K. The experimental results were analysed in the light of Bloomfield and Dewan's theory. The analysis showed that the theory correctly predicts the sign of viscosity function in the case of benzene + benzonitrile and cyclohexane + methylpropylketone.

Keywords. Excess viscosity; absolute rate theory; free volume theory; Flory theory; residual excess entropy; Bloomfield-Dewan theory.

1. Introduction

Bloomfield and Dewan (1971) developed a theoretical expression between viscosity and thermodynamic properties of mixing on the basis of absolute rate and free volume theories of flow. The applicability of this equation to binary mixtures of non-polar components was examined using viscosity data (Bloomfield and Dewan 1971; Delmas *et al* 1975). The analyses showed that the equation is applicable to binary mixtures of non-polar components when the free volume difference between the components is very small. However, no effort has been made to test the applicability of the equation to binary mixtures containing one polar component. Hence, viscosities of binary mixtures, benzene + benzonitrile, benzene + methylpropylketone and cyclohexane + methylpropylketone were determined at 303.15 K and the results were analysed on the basis of Bloomfield and Dewan's expression.

2. Experimental

Viscosities of pure liquids and binary mixtures were determined using an Ostwald viscometer at 303.15 K. The results were accurate to ± 0.5 per cent. Densities were measured using a bicapillary pycnometer described earlier (Naidu and Krishnan 1965). Cyclohexane (BDH), benzene (BDH), and benzonitrile (Riedel) were purified by the methods reported earlier (Naidu and Krishnan 1965; Reddy and Naidu 1978). Methylpropylketone (Riedel) was dried over potassium carbonate for three days, then boiled for two hours and fractionally distilled. The purity of

the samples was checked by comparing the experimental density and boiling point data with those reported in the literature (Timmermans 1950).

3. Theoretical and calculations

According to Bloomfield and Dewan excess viscosity is given by

$$\begin{aligned} \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \\ = - \frac{\Delta G^R}{RT} + \frac{1}{\bar{v}} - 1 - \left(\frac{x_1}{\bar{v}_1 - 1} + \frac{x_2}{\bar{v}_2 - 1} \right) \end{aligned} \quad (1)$$

which can also be written as

$$\Delta \ln \eta_{th} = \ln \eta_H + \ln \eta_S + \ln \eta_V \quad (2)$$

where $\ln \eta_H$, $\ln \eta_S$ and $\ln \eta_V$ are the enthalpy, entropy and free volume contributions to the excess viscosity. Residual entropy of mixing, ΔS^R , and reduced volume, \bar{v} , are given by the Flory (1965) equations

$$\Delta S^R = - 3x_1 \frac{P_1^* V_1^*}{T_1^*} \ln \frac{\bar{v}_1^{1/3} - 1}{\bar{v}^{1/3} - 1} - 3x_2 \frac{P_2^* V_2^*}{T_2^*} \ln \frac{\bar{v}_2^{1/3} - 1}{\bar{v}^{1/3} - 1} \quad (3)$$

and

$$\bar{v} = V / (x_1 V_1^* + x_2 V_2^*) \quad (4)$$

The parameters in eqs (3) and (4) have the same significance as described by Flory (1965) and the values are given in table 2. The experimental excess enthalpies reported elsewhere (Amaya 1961; Tanaka *et al* 1974; Kiyohara and Benson 1977) and density values of this work were used for the calculation of enthalpies of mixing, ΔH^M and reduced volume \bar{v} . The expression

$$\Delta \ln \eta_{exp} = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (5)$$

gives the experimental excess viscosity.

Predicted and observed excess viscosities are presented in table 1. The experimental excess viscosities are fitted into an equation

$$\Delta \ln \eta_{exp} = x_1 x_2 [A_0 + A_1 (x_1 - x_2) + A_2 (x_1 - x_2)^2]. \quad (6)$$

The parameters A_0 , A_1 , and A_2 obtained by the method of least squares are given in table 3 along with the standard deviation σ ($\Delta \ln \eta_{exp}$).

4. Discussion

Predicted and observed excess viscosities included in table 1 show that Bloomfield and Dewan Theory correctly predicts the sign of excess viscosity in two binary mixtures, benzene+benzonitrile and cyclohexane+methylpropylketone. Further

Table 1. Calculated and experimental viscosities of liquid mixtures at 303.15 K.

x_1	ρ g cm ⁻³	η cp	$\ln \eta$	$\Delta \ln \eta_{th}$	$\Delta \ln \eta_{exp}$
<i>Benzene + benzonitrile</i>					
0.0000	0.99621	1.139	0.130
0.1527	0.97919	1.001	0.014	-0.016	-0.012
0.3165	0.96032	0.902	-0.103	-0.029	-0.017
0.4174	0.94813	0.831	-0.185	-0.035	-0.021
0.5485	0.93184	0.765	-0.268	-0.040	-0.024
0.6569	0.91751	0.715	-0.336	-0.037	-0.019
0.7859	0.90009	0.659	-0.417	-0.029	-0.011
0.9145	0.88124	0.607	-0.499	-0.015	-0.006
1.0000	0.86823	0.576	-0.552
<i>Benzene + methylpropylketone</i>					
0.0000	0.79669	0.466	-0.764
0.1304	0.80228	0.469	-0.757	0.017	-0.021
0.2771	0.81093	0.475	-0.744	0.024	-0.026
0.3294	0.81856	0.484	-0.726	0.031	-0.032
0.4869	0.82942	0.499	-0.695	0.030	-0.035
0.6257	0.83934	0.515	-0.664	0.024	-0.036
0.6946	0.84187	0.522	-0.650	0.019	-0.033
0.7707	0.84987	0.532	-0.631	0.012	-0.031
0.9042	0.86007	0.553	-0.592	0.001	-0.020
1.0000	0.86823	0.576	-0.552
<i>Cyclohexane + methylpropyl ketone</i>					
0.0000	0.79669	0.466	-0.764
0.1524	0.78940	0.474	-0.747	-0.196	-0.070
0.2942	0.78394	0.496	-0.704	-0.358	-0.106
0.3752	0.78086	0.507	-0.679	-0.413	-0.127
0.4326	0.78902	0.517	-0.659	-0.436	-0.141
0.5075	0.77684	0.532	-0.631	-0.450	-0.154
0.5951	0.77434	0.555	-0.589	-0.445	-0.162
0.7377	0.77098	0.607	-0.499	-0.386	-0.153
0.8891	0.76902	0.695	-0.364	-0.238	-0.104
1.0000	0.76892	0.826	-0.197

Table 2. Parameters of the pure components at 303.15 K.

Component	$a \times 10^8$	K_T	\bar{v}	V	V^*	P^*	T^*
	deg ⁻¹	TPa ⁻¹		cm ³ mol ⁻¹	cm ³ mol ⁻¹	J cm ⁻³	deg
Benzene	1.242	1019.4	1.299	89.81	69.12	623.4	4713.2
Cyclohexane	1.230	1189.8	1.297	109.48	84.42	527.2	4604.9
Benzonitrile	0.891	642.6	1.228	103.51	84.29	633.9	5622.0
Methylpropyl- ketone	1.192	1127.2	1.289	108.13	83.85	533.1	4811.1

Table 3. Least square parameters and the standard deviation of $\Delta \ln \eta_{app}$ at 303.15 K.

System	A_0	A_1	A_2	$\sigma(\Delta \ln \eta)$
Benzene + benzonitrile	-0.086	0.010	0.008	0.002
Benzene + methylpropylketone	-0.136	0.021	-0.112	0.001
Cyclohexane + methylpropylketone	-0.598	0.313	-0.330	0.003

the quantitative agreement between predicted and observed excess viscosity values is better in the former mixture. The theory fails to predict the sign of viscosity function over the whole range of composition in benzene+methylpropylketone mixture. The inapplicability of the theory in this case cannot be ascribed to large difference in free volumes as the difference is very small.

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