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BINARY LIQUID MIXTURES OF ACETONITRILE WITH METHYL, ETHYL, n-PROPYL AND n-BUTYL BENZOATES. VARIATION OF VISCOSITIES WITH TEMPERATURE AND COMPOSITION

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ABSTRACT

Viscosity values of the binary mixtures: (I) acetonitrile + methylbenzoate; (II) acetonitrile + ethyl benzoate; (III) acetonitrile + n-propyl benzoate and (IV) acetonitrile + n-butyl benzoate at 10, 20, 30, 40 and 50 °C have been measured. Several equations for the variation of viscosity with temperature and composition of the mixtures are proposed; the effect of chain length of the esters has also been studied.

INTRODUCTION

Viscosity is recognised as having a decisive influence on transport phenomena, which makes knowledge of its value important for many systems, especially for the study of mass transference phenomena. The viscosity of many liquids varies with temperature in accordance with the equation

$$\eta = A \exp(B/T) \tag{1}$$

The interpretation of this behaviour is kinetic and requires an acceptance that the fundamental reason for the viscosity of liquids is the existence of intermolecular forces which give these substances the character of a condensed state. The way the viscosity of liquid mixtures varies with their composition permits interpretation of the nature of the forces acting on their molecules [1,2].

EXPERIMENTAL

Viscosity measurements were made with an Ostwald viscosimeter calibrated with distilled water at different temperatures, with the density and viscosity values being taken from the literature [3]. Timings were made with a chronometer to an accuracy of ±0.01; by repeating the successive measurements under identical conditions, it was possible to calculate the viscosity to within a margin of error of ±0.004 cP. Temperature was kept constant within ±0.05 °C by means of a thermostat, heater and refrigerator, with the viscosimeter kept in vertical position throughout.

The following reagents were used: acetonitrile Panreac 99.5%, methyl benzoate Fluka 99%; these were purified by suitable procedures involving distillation and drying [4]; n-propyl and n-butyl benzoates were synthesized by a Fisher esterification [5]; the use of a Dean–Stark apparatus, to remove water from the reaction, reduced the reflux time from 10 h [5] to 5. The ester obtained was washed with water and extracted with ether; anhydrous Na_2SO_4 was used for drying and $NaHCO_3$ to eliminate the excess benzoic acid; the purification was carried out in a vacuum line within a range of 122–124 °C for n-propyl benzoate and 156–158 °C for n-butyl benzoate.

Characterization of the esters was carried out with an RMN-H1 Spectrometer model R-24B, 60 MHz Hitachi–Perkin-Elmer and a Hewlett Packard 3390A integrator with a Perkin-Elmer 990 gas chromatograph; purity was assessed with a column in liquid phase over a solid Supelcoport 100/120, 1–1/8″, the working temperatures being 250, 275 and 150 °C for the detector, injector and oven, respectively; the carrier gas was nitrogen at 20 $cm^3\ min^{-1}$, and combustion gases were air and hydrogen at 240 and 30 $cm^3\ min^{-1}$, respectively. The purity was 99.95% for both esters.

Mixtures were prepared by mixing weighed amounts of the pure liquids and care was taken to prevent evaporation.

RESULTS

Table 1 shows the variation of viscosity with temperature and composition of the mixtures; the dependence of viscosity on temperature conforms to an equation of the type

$$\ln \eta = \ln A + B/T \qquad (2)$$

TABLE 1

Coefficients of the polynomial variation of B with the composition of the mixtures I, II, III and IV

Mixture	b_0	b_1	b_2	b_3	R [a]	σ_x [b]
I	858.61	328.25	−248.50	1037.70	0.9990	0.626
II	859.59	319.83	60.97	808.43	0.9987	0.645
III	859.37	493.95	−176.99	1066.50	0.9974	1.133
IV	858.95	419.60	329.49	681.64	0.9988	0.787

[a] R = multilinear correlation coefficient.

[b] $\sigma_x = \left[\Sigma \frac{(X_{obs} - X_{calc})^2}{(n_{obs} - n)}\right]^{1/2}$ = standard deviation.

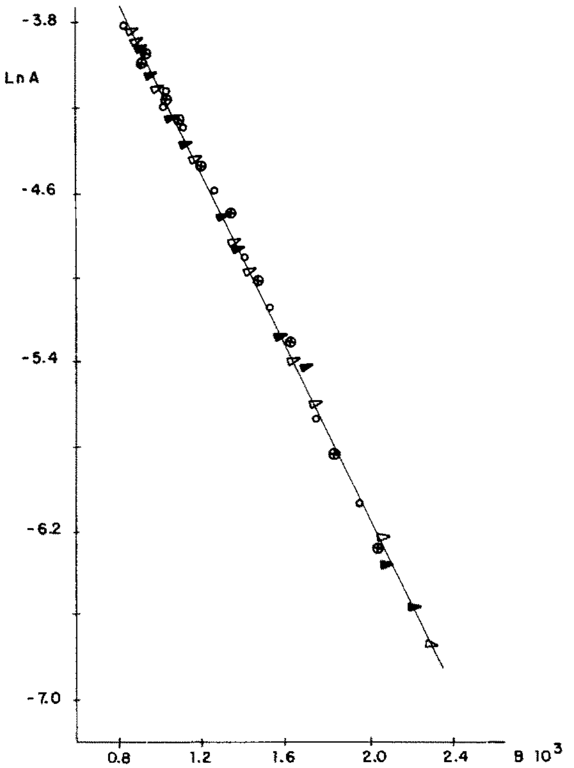

Fig. 1. Variation of ln A vs. B for mixtures I (○), II (⊕), III (▲) and IV (△).

where the parameters A and B depend on the nature of the mixture and of its composition. In turn, the polynomial variation of B (Fig. 1) with the composition of the mixtures is of the form

$$B = b_0 + b_1 X + b_2 X^2 + b_3 X^3 \tag{3}$$

X being the mole fraction of the esters, whereas the variation of ln A with B is constant for each of the four systems studied (Fig. 2)

$$\ln A = -0.002B - 2.077 \tag{4}$$

being $\sigma_x = 0.04$ and $R = 0.9990$. Table 1 contains coefficients of the variation of B with composition and Table 2 the equations for the variation of viscosity with the temperature and composition of the mixtures. With the purpose of studying the deviation of these systems with respect to ideal behaviour, Grumbey [6] (basing his study on the theory of regular solutions [7,8]) proposed the following empirical expression

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 \theta \tag{5}$$

where θ is a measurement of the non-ideal behaviour of the mixture, X_i

TABLE 2

Equations for the variation of viscosity with temperature and composition for mixtures I, II, III and IV

I	$\ln \eta = (-3.79 + 858.61/T) + X(-0.66 + 328.35/T) + X^2(0.50 - 248.50/T) + X^3(-2.07 + 1037.70/T)$
II	$\ln \eta = (-3.80 + 859.59/T) + X(-0.64 + 319.83/T) + X^2(-0.12 + 60.97/T) + X^3(-1.62 + 808.43/T)$
III	$\ln \eta = (-3.80 + 859.37/T) + X(-0.99 + 493.95/T) + X^2(0.35 - 176.99/T) + X^3(-2.12 + 1060.50/T)$
IV	$\ln \eta = (-3.80 + 858.95/T) + X(-0.84 + 419.60/T) + X^2(-0.66 + 329.49/T) + X^3(-1.36 + 681.64/T)$

TABLE 3

Experimental values of η and θ at different compositions and temperatures for mixtures of acetonitrile and I (methyl benzoate), II (ethyl benzoate), III (n-propyl benzoate) and IV (n-butyl benzoate)

X_1	10 °C		20 °C		30 °C		40 °C		50 °C	
	η	θ	η	θ	η	θ	η	θ	η	θ
Mixture I										
0.000	0.452	–	0.408	–	0.371	–	0.339	–	0.309	–
0.134	0.491	−1.22	0.444	−1.05	0.400	−0.98	0.365	−0.85	0.329	−0.82
0.255	0.527	−1.45	0.476	−1.24	0.430	−1.12	0.387	−1.05	0.351	−0.93
0.373	0.580	−1.62	0.515	−1.44	0.460	−1.33	0.410	−1.26	0.367	−1.16
0.480	0.702	−1.68	0.624	−1.45	0.551	−1.36	0.500	−1.17	0.446	−1.07
0.570	0.766	−1.76	0.676	−1.49	0.595	−1.36	0.521	−1.26	0.467	−1.08
0.666	0.934	−1.78	0.805	−1.52	0.695	−1.40	0.608	−1.25	0.531	−1.13
0.752	1.131	−1.87	0.958	−1.58	0.814	−1.48	0.701	−1.33	0.602	−1.22
0.837	1.370	−2.21	1.128	−1.92	0.950	−1.77	0.811	−1.55	0.691	−1.40
0.922	1.864	−1.89	1.508	−1.40	1.226	−1.48	1.016	−1.34	0.854	−1.13
1.000	2.435	–	1.879	–	1.523	–	1.238	–	1.016	–
Mixture II										
0.129	0.515	−0.85	0.465	−0.67	0.416	−0.65	0.378	−0.57	0.340	−0.56
0.250	0.550	−1.29	0.496	−1.08	0.444	−0.99	0.403	−0.86	0.362	−0.80
0.362	0.632	−1.29	0.554	−1.17	0.495	−1.04	0.443	−0.93	0.397	−0.84

0.469	0.711	−1.47	0.627	−1.28	0.551	−1.16	0.491	−1.02	0.436	−0.94
0.571	0.828	−1.60	0.714	−1.43	0.621	−1.30	0.549	−1.14	0.485	−1.03
0.657	0.989	−1.62	0.843	−1.44	0.721	−1.31	0.631	−1.13	0.550	−1.03
0.756	1.271	−1.59	1.056	−1.39	0.897	−1.20	0.764	−1.06	0.659	−0.94
0.832	1.637	−1.20	1.362	−0.88	1.120	−0.78	0.939	−0.64	0.799	−0.53
0.914	2.208	−0.15	1.764	−0.06	1.418	−0.08	1.161	−0.18	0.972	−0.26
1.000	2.597	–	2.013	–	1.597	–	1.284	–	1.058	–
Mixture III										
0.127	0.488	−1.63	0.439	−1.45	0.397	−1.32	0.362	−1.20	0.326	−1.15
0.247	0.533	−1.82	0.480	−1.58	0.430	−1.46	0.386	−1.33	0.346	−1.29
0.362	0.619	−1.82	0.544	−1.64	0.484	−1.50	0.431	−1.40	0.386	−1.29
0.467	0.702	−2.05	0.614	−1.82	0.540	−1.67	0.479	−1.53	0.424	−1.42
0.567	0.887	−1.95	0.755	−1.75	0.654	−1.60	0.570	−1.48	0.499	−1.36
0.658	1.044	−2.22	0.879	−1.99	0.749	−1.82	0.652	−1.64	0.564	−1.53
0.748	1.344	−2.29	1.113	−2.00	0.929	−1.84	0.786	−1.70	0.670	−1.60
0.842	1.797	−2.49	1.522	−1.79	1.237	−1.65	1.025	−1.52	0.853	−1.46
0.928	2.686	−2.27	2.048	−1.50	1.609	−1.63	1.307	−1.40	1.075	−1.30
1.000	3.451	–	2.586	–	2.013	–	1.604	–	1.301	–
Mixture IV										
0.125	0.490	−1.68	0.446	−1.41	0.402	−1.31	0.364	−1.22	0.313	−1.19
0.244	0.546	−1.79	0.486	−1.62	0.434	−1.49	0.392	−1.37	0.352	−1.28
0.355	0.601	−2.48	0.533	−1.84	0.472	−1.70	0.424	−1.55	0.382	−1.40
0.463	0.728	−2.82	0.629	−1.87	0.551	−1.71	0.483	−1.61	0.430	−1.47
0.563	0.895	−2.09	0.762	−1.90	0.655	−1.75	0.567	−1.63	0.461	−1.81
0.654	1.140	−2.06	0.956	−1.84	0.808	−1.69	0.696	−1.53	0.603	−1.39
0.750	1.436	−2.35	1.173	−2.12	0.979	−1.93	0.825	−1.78	0.667	−1.90
0.830	1.954	−2.15	1.570	−1.85	1.270	−1.72	1.056	−1.54	0.900	−1.26
0.919	2.775	−1.81	2.131	−1.72	1.690	−1.56	1.368	−1.38	1.119	−1.26
1.000	3.802	–	2.835	–	2.189	–	1.730	–	1.388	–

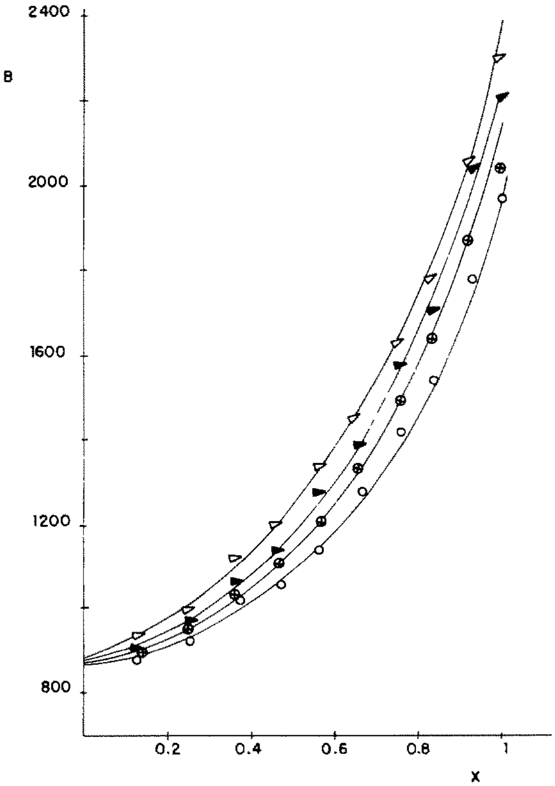

Fig. 2. Variation of parameter *B* with ester concentration for mixtures I (○), II (⊕), III (▲) and IV (△).

represents the mole fraction of the esters, η_i the viscosity of the pure liquids and η the viscosity of the mixtures. Table 3 shows the values for η and θ calculated for the various systems.

DISCUSSION

The variation of η with ester concentration shows a negative deviation with respect to ideal behaviour, which would be characterised by a linear variation. This behaviour indicates the existence of dispersion forces between the molecules of the mixtures [1,2]. The high values for θ reveal, moreover, a marked deviation with respect to ideal behaviour, a deviation which becomes smaller as the temperature increases; the variation of θ with X_i shows in each case a minimum value which depends on the ester of the mixture. Grumbey justifies the behaviour of the viscosity of the binary liquid mixtures in terms of an energy interchange defined by

$$\theta = (W/RT)\alpha_1(X_2 + (\alpha_2/\alpha_1)X_1) \tag{6}$$

where W is the interchange energy arising from the increase in lattice energy due to the juxtaposition of molecule 1 into the lattice of molecule 2; the parameters α_1 and α_2 are calculated by means of the vapour pressures P_0 of components 1 and 2, in accordance with

$$d(\ln \eta)/d(\ln P_0) = \alpha \tag{7}$$

However, eqn. (6) is deduced from the theory of regular solutions, in which specific molecular interactions are not taken into account. In this way, a study has recently been made [9] of the viscosity of binary liquid mixtures of *N*-methylpyrrolidinone–tetrahydrofuran and propylene carbonate–acetonitrile and it has been shown that the behaviour of these liquid mixtures cannot be explained merely in terms of energy interchanges such as that defined by eqn. (6). However, in the present work the high values of θ allow us to suppose the existence of strong dispersion forces, due partly to the size of the ester molecules and partly to the different polarity of the liquids of the mixture (acetonitrile $\mu = 3.40$ D and benzoates $\mu \simeq 1.90$ D), so that the possible interactions between dipoles of acetonitrile will be dispersed by the presence of the ester molecules. The values of θ do not permit a quantitative interpretation of these facts, since there is no relation between them and the size of the molecules; however, the way in which the viscosity varies with composition allows us to conclude that the dispersion forces are intense and decrease in the mixtures in the order IV > III > II > I, at any temperature.

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