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Viscosities of Nonelectrolyte Liquid Mixtures. II. Binary Mixtures of *n*-Hexane with Alkanoates and Bromoalkanoates

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Viscosity measurements are reported for mixtures of ethyl ethanoate, ethyl propionate, ethyl butyrate, ethyl-2-bromopropionate, ethyl-3-bromopropionate, ethyl-2-bromobutyrate, and ethyl-4-bromobutyrate with *n*-hexane at 303.15 K. The viscosity data have been correlated with equations of Grunberg and Nissan, of McAllister, and of Auslaender. Furthermore, excess Gibbs energies of activation ΔG^{*E} of viscous flow have been calculated with Eyring's theory of absolute reaction rates and values of ΔG^{*E} for the present binary mixtures have been explained in terms of the dipole–dipole interaction in alkanoates and the intramolecular Br...O interaction in bromoalkanoates.

KEY WORDS: activation energy; alkanoates; binary mixtures; bromoalkanoates; Gibbs energy of activation; *n*-hexane; molecular interactions; viscosity.

1. INTRODUCTION

Recently, interest in the study of the thermodynamic properties of liquid mixtures containing an alkanoate as one of the components has increased [1–14]. Such studies are of great significance because one obtains information regarding the structural changes which occur in the pure alkanoate because of mixing. Alkanoates, though, possess high dipole moments but behave like normal liquids. Otin et al. [15] reported excess enthalpies for a series of alkanoate and bromoalkanoate mixtures with hexane. The excess enthalpies are quite dependent on the size of the alkanoate molecules and decrease as the alkyl chain length in alkanoate is increased. It is also observed that the intramolecular Br...O interaction increases as

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the distance of separation between the bromine atom and the carboxylate group decreases.

Measurements of the viscosity of binary mixtures also reveal information about the molecular packing, the molecular motion, and various types of intermolecular interactions as related to the size, shape, and chemical nature of the component molecules [16–19]. Therefore, to gain further insight into the molecular interactions in such systems, viscosity measurements have been undertaken. In this paper, we report viscosities of mixtures of ethyl ethanoate (EE), ethyl propionate (EP), ethyl butyrate (EB), ethyl-2-bromopropionate (E2BrP), ethyl-3-bromopropionate (E3BrP), ethyl-2-bromobutyrate (E2BrB), and ethyl-4-bromobutyrate (E4BrB) with *n*-hexane (n-C_6).

2. EXPERIMENTS

The measurements of viscosity η at 303.15 K were made with a modified Ubbelohde suspended-level viscometer. The viscometer was designed so as to reduce surface tension effects to negligible values [20]. The efflux time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a resolution of 0.1 s. Flow time for doubly distilled water was more than 210 s. In the experiment, the viscometer was suspended vertically for a sufficient time in a constant-temperature bath maintained at (303.15 ± 0.02) K. Doubly distilled water and purified benzene were used for the calibration of the viscometer. The densities ρ of the pure components and the binary mixtures at 303.15 K required for converting kinematic viscosities into absolute viscosities were measured with an Anton–Paar KG densimeter (Model DMA 60/602). The details of the procedure of measuring the viscosity and density have been described in our previous papers [8, 19, 21]. The errors in η and ρ are estimated to be 0.002 mPa · s and 0.02 $kg \cdot m^{-3}$, respectively.

Samples of *n*-hexane, ethyl ethanoate, ethyl propionate, ethyl butyrate (purity, >99%), ethyl-2-bromopropionate, ethyl-3-bromopropionate, ethyl-2-bromobutyrate, and ethyl-4-bromobutyrate (purity, >97%) were obtained from Fluka AG or Merck Schuchardt. *n*-Hexane, ethyl propionate, and ethyl butyrate were dried over molecular sieve beads, type 4A (from Fluka), and were fractionally distilled before use. The bromoalkanoates were used directly because of the difficulty of carrying out a perfect distillation of them [15]. The purity of the above liquids was checked by measuring the boiling point, density, and refractive index. The measured values were found to be in good agreement with reliable literature values [22, 23] as shown in Table I.

Table I. Density and Refractive Index of the Pure Liquids

Liquid	Temp. (K)	Density ($kg \cdot m^{-3}$)		Refractive index	
		Expt.	Lit.	Expt.	Lit.
EE	303.15	888.55	888.51 [22]	1.3673	1.3672 [22]
EP	303.15	879.14	879.03 [22]	1.3795	1.3790 [22]
EB	303.15	868.83	868.71 [22]	1.3876	1.3881 [22]
E2BrP	293.15	1389.45	1394.00 [23]	1.4459	1.449 [23]
E3BrP	293.15	1407.64	1412 [23]	1.4524	1.452 [23]
E2BrB	293.15	1327.61	1328 [23]	1.4480	1.447 [23]
E4BrB	293.15	1362.67	1363 [23]	1.4549	1.456 [23]
n-C_6	303.15	650.54	650.6 [22]	1.3699	1.3696 [22]

3. RESULTS

The experimental viscosities η at 303.15 K and mole fractions x_1 of alkanoates for the binary mixtures EE + n-C_6, EP + n-C_6, EB + n-C_6, E2BrP + n-C_6, E3BrP + n-C_6, E2BrB + n-C_6, and E4BrB + n-C_6 are listed in Table II. A polynomial of the type

$$\eta = \sum_{i=0}^{m} A_i x_1^i \tag{1}$$

was fitted to the data for each mixture by the method of least squares, with all points weighted equally. Values of the parameters A_i and the standard deviations σ are given in Table III. Plots of the results for η and their representations by Eq. (1) are given in Fig. 1. It is evident from Fig. 1 that η increases with the mole fraction x_1 of alkanoates for all seven binary systems. Figure 1 reveals that the viscosities exhibit negative deviations from a linear dependence on the mole fractions over the entire range of composition for all binary mixtures. Somewhat similar negative deviations were observed earlier for mixtures of alkyl alkanoates with *n*-heptane [24].

The negative deviations suggest a loss of cohesive energy upon mixing the pure components, which in the present case may be associated with the disruption of dipolar forces existing in alkanoate molecules. The negative deviations increase in the following order:

(i) EE > EP > EB,
(ii) EP $\ll$ E2BrP < E3BrP,
(iii) EB $\ll$ E2BrB < E4BrB.

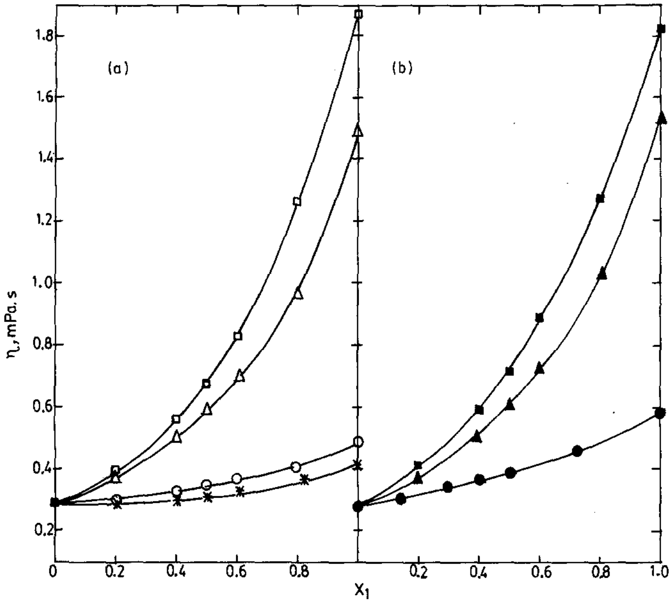

Fig. 1. Dependence of viscosity η at 303.15 K on the mole fraction x_1 of alkanoate for binary mixtures: (a) EE (∗), EP (○), E2BrP (△), and E3BrP (□); (b) EB (●), E2BrB (▲), and E4BrB (■) with *n*-hexane.

Table II: Viscosity and Excess Gibbs Energy of Activation of Viscous Flow for Binary Mixtures at 303.15 K as a Function of the Mole Fraction x_1 of Alkanoates

x_1	η (mPa · s)	ΔG^{*E} ($J \cdot mol^{-1}$)
	EE + n-C_6	
0.0000	0.2859	—
0.2032	0.2874	−141
0.4017	0.3009	−191
0.5013	0.3117	−194
0.5990	0.3249	−180
0.8203	0.3611	−131
1.0000	0.4104	—
	EP + n-C_6	
0.0000	0.2859	—
0.1832	0.2997	−114
0.3971	0.3276	−166
0.4989	0.3451	−168
0.5988	0.3661	−153
0.8005	0.4138	−116
1.0000	0.4833	—

Table II. *(Continued)*

x_1	η (mPa · s)	ΔG^{*E} ($J \cdot mol^{-1}$)
	EB + n-C_6	
0.0000	0.2859	—
0.1354	0.3067	−57
0.2995	0.3404	−82
0.3884	0.3564	−124
0.4879	0.3880	−87
0.7244	0.4602	−79
1.0000	0.5776	—
	E2BrP + n-C_6	
0.0000	0.2859	—
0.1996	0.3720	−151
0.4039	0.5117	−192
0.5022	0.5973	−221
0.5991	0.7048	−218
0.7961	1.0118	−185
1.0000	1.4931	—
	E3BrP + n-C_6	
0.0000	0.2859	—
0.2142	0.3919	−206
0.4043	0.5500	−256
0.5019	0.6740	−206
0.6029	0.8315	−154
0.8046	1.2634	−60
1.0000	1.8673	—
	E2BrB + n-C_6	
0.0000	0.2859	—
0.1972	0.3726	−139
0.3889	0.5074	−191
0.4924	0.6029	−201
0.5981	0.7246	−189
0.7949	1.0325	−126
1.0000	1.5290	—
	E4BrB + n-C_6	
0.0000	0.2859	—
0.2012	0.4062	−38
0.3949	0.5871	−21
0.4988	0.7248	13
0.6008	0.8853	33
0.7973	1.2736	35
1.0000	1.8264	—

Table III: Coefficients A_i in Eq. (1) for η (mPa · s) and in Eq. (3) for $\Delta \ln \eta$ and $\Delta G^{*E}/RT$ at 303.15 K

Property	A_0	A_1	A_2	A_3	$10^3\sigma$
Ethyl ethanoate + *n*-hexane					
η	0.2853	−0.0067	0.1105	0.0200	3.8
$\Delta \ln \eta$	−0.3767	−0.0061	−0.1256		3.0
$\Delta G^{*E}/RT$	−0.3039	−0.0043	−0.1199		2.4
Ethyl propionate + *n*-hexane					
η	0.2848	0.0911	0.0030	0.1028	3.8
$\Delta \ln \eta$	−0.2900	−0.0111	−0.0818		2.0
$\Delta G^{*E}/RT$	−0.2630	−0.0128	−0.0832		2.4
Ethyl butyrate + *n*-hexane					
η	0.2852	0.1389	0.1194	0.0338	2.8
$\Delta \ln \eta$	−0.1560	−0.0188	−0.0825		2.7
$\Delta G^{*E}/RT$	−0.1609	−0.0254	−0.0235		8.4
Ethyl-2-bromopropionate + *n*-hexane					
η	0.2843	0.4441	−0.0658	0.8293	4.3
$\Delta \ln \eta$	−0.3444	0.0668	−0.1739		2.0
$\Delta G^{*E}/RT$	−0.3372	0.0708	−0.2134		3.5
Ethyl-3-bromopropionate + *n*-hexane					
η	0.2862	0.3656	0.4055	0.8130	2.0
$\Delta \ln \eta$	−0.3318	−0.3378	0.1528		4.1
$\Delta G^{*E}/RT$	−0.3381	−0.4350	0.0558	0.4406	3.0
Ethyl-2-bromobutyrate + *n*-hexane					
η	0.2837	0.4549	−0.0185	0.8068	6.1
$\Delta \ln \eta$	−0.2915	−0.0514	−0.1156		1.2
$\Delta G^{*E}/RT$	−0.3154	−0.0323	−0.0325		1.1
Ethyl-4-bromobutyrate + *n*-hexane					
η	0.2857	0.4583	0.5999	0.4816	6.1
$\Delta \ln \eta$	0.0322	−0.2689	−0.0674	0.3030	2.7
$\Delta G^{*E}/RT$	0.0152	−0.2189	−0.0552	0.1922	1.9

In addition, the excess viscosities $\Delta \ln \eta$ were calculated from the Arrhenius equation

$$\Delta \ln \eta = \ln \eta/\eta_2^0 - x_1 \ln \eta_1^0/\eta_2^0 \tag{2}$$

where η_i^0 represents the viscosity of pure component i. The values of $\Delta \ln \eta$ for all the mixtures were filtered to a Redlich–Kister [25] polynomial equation,

$$\Delta \ln \eta = x_1 x_2 \sum_{i=0}^{m} A_i(1-2x_1)^i \tag{3}$$

Values of the coefficient A_i and the standard deviations σ are recorded in Table III. Plots of the results of $\Delta \ln \eta$ and their representations by Eq. (3) are shown in Fig. 2.

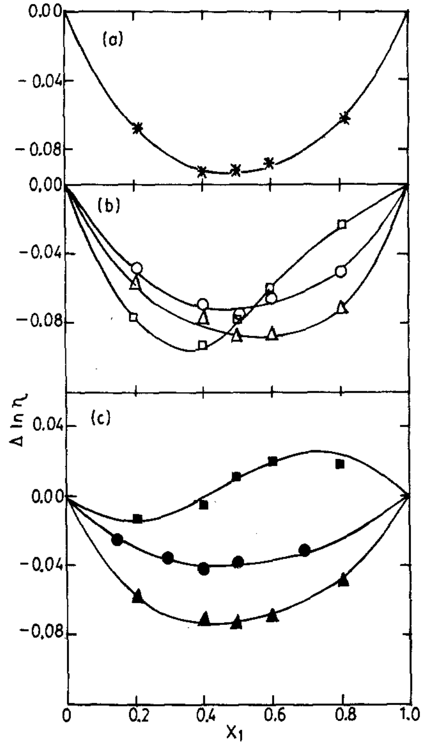

Fig. 2. Dependence of excess viscosity $\Delta \ln \eta$ where η is in mPa·s) at 303.15 K on the mole fraction x_1 of alkanoate for binary mixtures. Symbols as in Fig. 1.

The excess viscosities $\Delta \ln \eta$ are negative for all the mixtures except for ethyl-4-bromobutyrate + *n*-hexane. For the ethyl-4-bromobutyrate + *n*-hexane mixture, small but negative values of $\Delta \ln \eta$ are observed only when the alkanoate mole fraction in the mixture is less than 0.4. Otherwise, small but positive deviations are observed.

4. CORRELATING EQUATIONS

There are currently increasing demands for the accuracy of predicting liquid-mixture viscosity for industrial applications. Therefore, it is desirable to have equations that are predictive in nature. The viscosities of liquid mixtures in terms of pure component data have been correlated by many investigators [26–28]. In this work, the Grunberg–Nissan [29], McAllister [30], and Auslaender [31] equations have been employed to correlate the present viscosity results.

The Grunberg and Nissan equation [29]

$$\ln \eta = x_1 \ln \eta_1^0 + x_2 \ln \eta_2^0 + x_1 x_2 G_{12} \tag{4}$$

gave the best overall fit among the 25 single-parameter equations tested for representing the viscosities of over 300 binary systems [26]. In Eq. (4), G_{12} is an adjustable parameter, also referred to as an interaction parameter [32].

We analyze Eq. (4) in two ways: (i) by calculating G_{12} for each of the binary mixtures at each individual composition and (ii) by calculating one optimum value of G_{12} for each binary mixture using all the experimental points.

The McAllister equation [30] based on Eyring's theory of absolute reaction rates and the three-body interaction model is

$$\begin{aligned}\ln \nu = {} & x_1 \ln \nu_1^0 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2^0 \\ & - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(2/3 + M_2/3M_1) \\ & + 3x_1 x_2^2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1)\end{aligned} \tag{5}$$

where Z_{12} and Z_{21} are interaction parameters and M_i and ν_i^0 are the molecular mass and kinematic viscosity of pure component *i*.

A three-parameter equation, due to Auslaender [31], has the form

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1^0) + A_{21}(B_{21}x_1 + x_2)(\eta - \eta_2^0) = 0 \tag{6}$$

where B_{12}, B_{21}, and A_{21} are the parameters representing binary interactions.

Table IV. Values of the Parameters in Eqs. (4) to (6) and Standard Percentage Deviations

	Eq. (4)		Eq. (5)			Eq. (6)			
Mixture	G_{12}	$\sigma(\%)$	Z_{12}	Z_{21}	$\sigma(\%)$	B_{12}	B_{21}	A_{21}	$\sigma(\%)$
EE + n-C_6	−0.398	0.50	0.408	0.401	0.50	−0.200	5.663	0.449	0.29
EP + n-C_6	−0.304	0.37	0.466	0.428	0.37	0.040	6.489	0.322	0.25
EB + n-C_6	−0.196	0.72	0.556	0.461	0.74	−0.100	−11.964	−0.150	0.78
E2BrP + n-C_6	−0.418	1.85	0.615	0.513	1.49	−0.452	−2.162	−1.384	0.70
E3BrP + n-C_6	−0.304	2.60	0.875	0.473	0.62	1.110	0.433	4.579	0.41
E2BrB + n-C_6	−0.322	0.66	0.698	0.501	0.49	0.175	3.690	0.701	0.22
E4BrB + n-C_6	0.029	1.58	0.935	0.556	0.18	0.797	0.745	2.570	0.36

The results of the three correlating equations, Eqs. (4)–(6), are compiled in Table IV. In Table IV, the second column provides G_{12} of Eq. (4), and the fourth and fifth columns list Z_{12} and Z_{21} of Eq. (5), while the seventh to ninth columns present the values of B_{12}, B_{21}, and A_{12} of Eq. (6). The values of the different parameters listed in Table IV were obtained from the experimental viscosity data by the method of least squares, assigning equal weights to each point.

The calculated values of G_{12} for Eq. (4) as a function of composition x_1 for each of the mixtures are plotted in Fig. 3. In general, G_{12} varies with

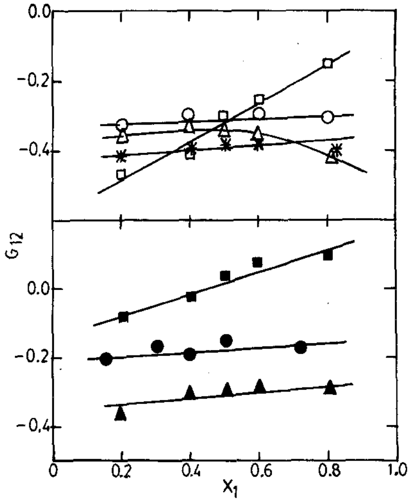

Fig. 3. Variation of Grunberg–Nissan parameter G_{12} of Eq. (4) with the mole fraction x_1 of alkanoate for binary mixtures. Symbols as in Fig. 1.

the composition for all the present mixtures. However, the variation in G_{12} is smaller for the mixtures containing ethyl alkanoates compared with the mixtures involving ethyl bromoalkanoates.

Furthermore, the correlating ability of each of the equations (4) to (6) is tested by calculating the standard percentage deviations $\sigma\%$ between the experimental and the calculated viscosity as

$$\sigma\% = \left\{ \frac{1}{n-k} \sum \left[\frac{100(\eta_{\text{exp}} - \eta_{\text{cal}})}{\eta_{\text{exp}}} \right]^2 \right\}^{1/2} \tag{7}$$

where n represents the number of data points and k the number of numerical coefficients in respective equations. The values of the standard percentage deviations for each of the equations are also given in Table IV. The values of σ (%) are in the range from 0.37 to 2.60 for Eq. (4), from 0.18 to 1.49 for Eq. (5), and from 0.22 to 0.98 for Eq. (6). The average values of $\sigma\%$ for Eq. (4), Eq. (5), and Eq. (6) are 1.18 ± 0.78, 0.63 ± 0.39, and 0.43 ± 0.21, respectively. From this study, it can be concluded that the correlating ability decreases in the order Auslaender > McAllister > Grunberg-Nissan equations. This is quite reasonable, and as expected since the number of coefficients is increased, the fitting has to be improved.

5. ACTIVATION ENERGY OF VISCOUS FLOW

On the basis of the theory of absolute reaction rates, the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from [19]

$$\Delta G^{*E}/RT = \ln(\eta V/\eta_2^0 V_2^0) - x_1 \ln(\eta_1^0 V_1^0/\eta_2^0 V_2^0) \tag{8}$$

where η and V are the viscosity and molar volume for the mixture and η_i^0 and V_i^0 are the viscosity and molar volume for pure component i, respectively. These results are also included in Table II. The estimated accuracy of ΔG^{*E} is about $20\ \text{J} \cdot \text{mol}^{-1}$. A polynomial of the type Eq. (3) was fitted to the $\Delta G^{*E}/RT$ results for each mixture. The values of the coefficients A_i and the standard deviations σ are also included in Table III. The plots of the results of ΔG^{*E} and their representation by Eq. (3) are shown in Fig. 4.

5.1. Alkanoates + *n*-Hexane Mixtures

The values of ΔG^{*E} as shown in Table II and Fig. 4 are negative for all three mixtures, which may be attributed to the dilution of dipole–dipole interactions in pure alkanoates. The negative values of ΔG^{*E} decrease in the order ethanoate > propionate > butyrate. Considering the more

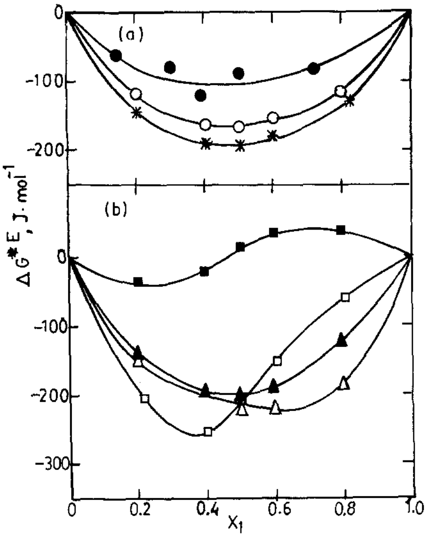

Fig. 4. Variation of excess Gibbs energy of activation ΔG^{*E} of viscous flow with composition for (a) ethyl alkanoate + *n*-hexane and (b) ethyl bromoalkanoate + *n*-hexane at 303.15 K. Symbols as in Fig. 1.

negative values of ΔG^{*E} as an indicator of the strength of disruption of the dipolar order of alkanoate, then the present variation of ΔG^{*E} for mixtures containing different ethyl alkanoates confirms the finding from the measurements of H^E and V^E for these mixtures that the polarity of alkanoate is diluted as the size of alkanoate is increased and their interactions therefore weaken [8, 13–15, 33, 34].

5.2. Bromoalkanoate + *n*-Hexane Mixtures

Figure 4 and Table II reveal that the values of ΔG^{*E} for mixtures of ethyl-2-bromopropionate, ethyl-3-bromopropionate, and ethyl-2-bromobutyrate with *n*-hexane are negative, while for the mixture ethyl-4-bromobutyrate + *n*-hexane both small negative and small positive values are observed. The values of ΔG^{*E} vary as the distance of separation between Br and O of the carboxylate group is increased. Thus, the intramolecular Br...O interaction affects the values of ΔG^{*E} in the mixtures as observed in the case of H^E measurements [15].

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