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Kinematic Viscosities of 1,2-Ethanediol/1,4-Dioxane Binary Mixtures from −10 to +80 °C

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Mixture kinematic viscosities (ν) were measured for the 1,2-ethanediol/1,4-dioxane binaries, covering the whole miscibility field ($0 \leq X_1 \leq 1$), at 19 temperatures ranging from −10 to +80 °C. The experimental ν values were fitted by different equations, such as Grunberg–Nissan, McAllister, Auslander, Heric, and polynomial one, using pure component properties for the binaries studied. A comparison of the calculated and experimental data shows that all the selected equations can be safely employed to predict the dependence of ν on the composition and on the temperature of the system studied when no binary experimental data are available.

Some previous papers from our laboratories have been concerned with the physical[1—3] and thermodynamic properties[4—6] of binary solvent systems of technical and electroanalytical interest. Being 1,2-ethanediol (ED) the more polar component ($\mu_{\mathrm{ED}}=2.28$ D)[7] (1 D$=3.3356\times10^{-30}$ C m) and the common species in all these studies, for this work we have chosen its parent compound 1,4-dioxane (DX) in order to make a binary liquid mixture with a *quasi*-apolar cosolvent ($\mu_{\mathrm{DX}}=0.45$ D).[8]

Although both these components have a wide-spread range of technological applications, namely plastics, rubbers, polymer solvents, reaction media for hydrolysis processes, thermoregulator, etc.,[9] it appears us that their binary system has not been largely studied. Therefore, we report here an extensive study on viscometric properties of ED/DX solvent system.

We carried out measurements on the kinematic viscosities (ν) on the whole composition range, expressed by the ED mole fraction ($0 \leq X_1 \leq 1$), and working at 19 temperatures in the $-10 \leq t/^\circ\mathrm{C} \leq 80$ range, with thermal scanning of 5 °C. This extrathermodynamic property seems very interesting from the point of view of industrial and engineering applications; therefore its preliminary knowledge is very important factor for the resolution of fluidodynamic and carrier problems. In addition, the easy determination and the simple operativity that is required for the experimental measure of this quantity on real time, makes possible in many cases the on-line processes control, being viscometric properties strictly related to the composition of the evolving systems and depending on the advancement degree of processes and chemical reactions.

Experimental

Materials. The solvents 1,2-ethanediol and 1,4-dioxane (containing less than 0.10 and 0.05% of water by mass found by Karl–Fischer titrations, respectively) were Carlo Erba (Milan) high purity grade reagents.

The dioxane was further purified by double fractional distillation over $\mathrm{LiAlH_4}$ to eliminate the traces of acids and to reduce the water total amount. Both the solvents were stored over 3 Å Molecular Sieves for many days before use. The final purity of both solvents was checked by gas chromatography (99.5% the diol, 99.8% the dioxane) and confirms the absence of other significant organic components.

Apparatus and Procedures. The mixtures were prepared just before use by weight on a Mettler PM 4800 Δ-range balance, operating in a dry box to avoid the atmospheric moisture, and then preserved over 3 Å Molecular Sieves. The probable error in the ED mole fraction (X_1) is estimated to be less than 1.5×10^{-4}.

Viscosity measurements were performed using a Schott-Geräte AVS 400 viscosity- measuring system, equipped with a series of Ubbelhode viscometers, covering the $(0.6 \leq \nu \leq 300)\times10^{-6}$ m^2 s^{-1} range. In all the determinations the kinetic energy correction has been taken into account according to the method suggested by Hagenbach.[10] In all the cases the experiments were generally performed at least in five replicates for each composition and at each temperature and the results were averaged.

The experimental reproducibility of the viscosity measurements at each temperature and composition was ±0.2%, with a standard deviation $\sigma(\nu)=1.4\times10^{-3}$. The estimated accuracy (95% confidence interval) was $\pm4\times10^{-3}$.

The temperature control was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C in all the investigated temperature ranges. The thermal control was checked by a thermoresistance Pt 100 (Tersid, Milan) inserted into the measuring capillary, and collecting the resistance values by using a Wayne Kerr 6425 precision component analyzer.

Karl–Fischer titrations were performed with an automatic titration system (Crison model KF 431) equipped with a digital buret (Crison model 738).

Results and Discussion

Table 1 summarizes the kinematic viscosity values (ν) for the two pure species ED and DX, and for 9 their mixtures covering the whole miscibility field expressed by the 1,2-ethanediol mole fraction ($0 \leq X_1 \leq 1$), experimentally determined in the $-10 \leq t/^\circ\mathrm{C} \leq +80$ temperature range, working at 5 °C intervals. Table 1 appears lackening of some ν values because phase separation occurred.

These kinematic viscosity data were processed by means of several equations relating the mixture viscosities to those of pure components, in order to improve our knowledge about these semiempirical theories, and

Table 1. Experimental Kinematic Viscosities ($\nu/10^{-6}$ m^2 s) for 1,2-Ethanediol/1,4-Dioxane Solvent System at Various Temperatures

	X_1											
t/°C	1.0000	0.9321	0.8590	0.7792	0.6955	0.6037	0.5041	0.3950	0.2755	0.1441	0.0000	r_1/r_2[a)]
−10	98.94	66.24	48.88	35.81	22.14	13.59	—	7.167	—	—	—	
−5	71.09	49.93	37.03	27.08	18.23	11.27	8.033	5.853	3.679	—	—	—
0	52.42	38.12	28.46	20.89	14.99	9.346	6.771	4.869	3.265	2.385	—	—
5	39.54	29.70	22.35	16.45	12.43	7.854	5.757	4.124	2.905	2.121	—	—
10	30.44	23.40	17.75	13.16	10.36	6.651	4.938	3.538	2.577	1.898	—	—
15	23.89	18.72	14.33	10.72	8.708	5.680	4.251	3.084	2.299	1.710	1.383	0.935
20	19.04	15.12	11.76	8.863	7.364	4.866	3.692	2.706	2.059	1.554	1.272	0.932
25	15.44	12.39	9.738	7.435	6.261	4.211	3.236	2.405	1.847	1.414	1.171	0.930
30	12.66	10.28	8.161	6.322	5.361	3.674	2.854	2.150	1.664	1.297	1.084	0.927
35	10.49	8.612	6.909	5.405	4.634	3.224	2.540	1.943	1.515	1.196	1.007	0.925
40	8.806	7.301	5.894	4.679	4.031	2.854	2.267	1.762	1.381	1.106	0.9379	0.922
45	7.482	6.248	5.088	4.088	3.539	2.534	2.037	1.606	1.265	1.026	0.8775	0.919
50	6.434	5.414	4.432	3.595	3.130	2.277	1.844	1.473	1.171	0.9567	0.8233	0.916
55	5.532	4.704	3.885	3.181	2.783	2.050	1.678	1.357	1.088	0.8945	0.7752	0.914
60	4.777	4.136	3.429	2.833	2.487	1.857	1.535	1.249	1.017	0.8379	0.7298	0.911
65	4.192	3.668	3.049	2.539	2.246	1.696	1.412	1.161	0.9554	0.7885	0.6901	0.908
70	3.687	3.272	2.723	2.287	2.034	1.553	1.305	1.075	0.9060	0.7419	0.6555	0.905
75	3.278	2.926	2.450	2.068	1.855	1.433	1.212	1.002	0.8633	0.7015	0.6235	0.903
80	2.909	2.645	2.225	1.885	1.709	1.331	1.133	0.9362	0.8286	0.6619	0.5947	0.900

a) $r_1/r_2=(M_1\rho_2/M_2\rho_1)^{1/3}$.

for predictive calculations of the investigated property in correspondence of the experimental data gaps. For the aims of this work the kinematic viscosity was chosen rather than the absolute one, being the first not affected by the experimental errors associated with the density measurements. Thus, the final uncertainties that affect the different correlation procedures were associated to the viscometric determinations only.

However, in order to provide to the readers the possibility of calculating absolute viscosity values ($\eta=\rho\nu$), we report in Table 2 the fitted density data of the mixtures at various temperatures.

Grunberg–Nissan Equation. One of the earlier attempts to describe the viscosity of binary solvent systems in terms of the properties of the pure components appeared in the literature by Grunberg and Nissan.11) These authors provided a simple equation, containing one adjustment parameter, of the type:

$$\ln \nu = X_1 \ln \nu_1 + X_2 \ln \nu_2 + X_1 X_2 d. \tag{1}$$

In Eq. 1, ν_1 and ν_2 refer to the kinematic viscosities of the pure species having mole fractions X_1 and X_2, respectively.

The term X_1X_2d represents the shiftness from the ideal behavior of noninteracting components, and the parameter d is assumed as a measure of the strength of interactions between unlike molecules. Nevertheless, from recent studies, it has been shown that in some cases the parameter d may be correlated with the molar volume differences of the pure species and with the mixing entropy.12)

The d values for this solvent system are listed in Table 3, along with the standard deviations $\sigma(\ln \nu)$ at all the investigated temperatures. As one can see, the parameter d is always negative, and this fact could be attributed to the existence of dispersion forces of any kind intervening as specific interactions between unlike molecules in the mixtures. These forces appear very strong at the lowest temperatures, responsible of a large deviation from the ideal behavior, and become weaker as the temperature increases up to 80 °C, with a moderate shiftness from the noninteracting components.

This fitting equation reproduces the experimental data with an average uncertainty $\overline{\Delta\nu}$, evaluated as follows:

$$\overline{\Delta\nu} = \frac{1}{N} \sum_{N} |\nu_{\text{exptl}} - \nu_{\text{calcd}}|, \tag{2}$$

where N is the number of experimental points, equal to $\pm 0.1002\times10^{-6}$ m^2 s^{-1}.

McAllister Equation. Starting from Eyring theory13) of liquid viscosity and considering the local interactions between contiguous fluid layers which are in stationary motion and in a dynamic steady state, McAllister provided a model to correlate the liquid mixture viscosity to the properties of pure species.14)

In this representation, the author takes into account the rate gradient which involves activated units jumping between adjacent layers, and this motion has been treated as if the molecule (or other aggregate) was undergoing a chemical process.

According to Eyring's hypothesis of the "hole in the liquid", a shear stress forces an activated jumping unit into a hole while traversing an activation energy barrier. The following relationships were derived by McAllister

Table 2. Smoothed Densities (ρ/g cm^{-3}) for 1,2-Ethanediol/1,4-Dioxane Solvent System at Various Temperatures

	X_1										
t/°C	1.0000	0.9321	0.8590	0.7792	0.6955	0.6037	0.5041	0.3950	0.2755	0.1441	0.0000
−10	1.133654	1.128859	1.125267	1.116870	1.113549	1.104072	—	1.093879	—	—	—
−5	1.130407	1.125210	1.121478	1.112905	1.109460	1.099650	1.092058	1.088751	1.082751	—	—
0	1.127083	1.121570	1.117698	1.108941	1.105355	1.095256	1.087438	1.083630	1.077516	1.068247	—
5	1.123704	1.117931	1.113923	1.104972	1.101237	1.090878	1.082841	1.078511	1.072248	1.062708	—
10	1.120288	1.114285	1.110149	1.100994	1.097107	1.086507	1.078257	1.073392	1.066958	1.057149	—
15	1.116853	1.110625	1.106376	1.097003	1.092969	1.082135	1.073681	1.068270	1.061654	1.051579	1.039168
20	1.113411	1.106949	1.102599	1.092999	1.088823	1.077756	1.069105	1.063143	1.056344	1.046005	1.033642
25	1.109971	1.103253	1.098818	1.088978	1.084672	1.073364	1.064524	1.058010	1.051034	1.040435	1.028112
30	1.106539	1.099538	1.095032	1.084944	1.080517	1.068958	1.059935	1.052870	1.045729	1.034874	1.022554
35	1.103119	1.095805	1.091239	1.080897	1.076358	1.064537	1.055335	1.047722	1.040432	1.029323	1.016952
40	1.099709	1.092057	1.087439	1.076840	1.072196	1.060100	1.050724	1.042567	1.035144	1.023784	1.011298
45	1.096305	1.088299	1.083632	1.072778	1.068031	1.055651	1.046102	1.037406	1.029864	1.017257	1.005591
50	1.092902	1.084537	1.079818	1.068716	1.063864	1.051194	1.041470	1.032240	1.024592	1.012739	0.999838
55	1.089488	1.080779	1.075998	1.064661	1.059693	1.046734	1.036832	1.027070	1.019324	1.007225	0.994050
60	1.086051	1.077037	1.072173	1.060622	1.055518	1.042280	1.032191	1.021900	1.014055	1.001710	0.988249
65	1.082572	1.073321	1.068344	1.056607	1.051338	1.037840	1.027553	1.016732	1.008779	0.996185	0.982463
70	1.079032	1.069645	1.064513	1.052627	1.047152	1.033426	1.022926	1.011570	1.003488	0.990641	0.976726
75	1.075407	1.066024	1.060683	1.048695	1.042957	1.029049	1.018318	1.006417	0.998173	0.985067	0.971081
80	1.071671	1.062476	1.056856	1.044822	1.038753	1.024726	1.013737	1.001279	0.992823	0.979450	0.965578

Table 3. Coefficients and Standard Deviations $\sigma(\ln \nu)$ of Different Fitting Equations for 1,2-Ethanediol/1,4-Dioxane Solvent System at Various Temperatures

	Grunberg–Nissan		McAllister			Heric		
t/°C	d	$10^2\sigma(\ln \nu)$	ν_{12}	ν_{21}	$10^3\sigma(\ln \nu)$	β_{12}	β_{21}	$10^2\sigma(\ln \nu)$
15	−1.185	4.6	7.458	1.994	9.7	−1.157	0.5560	2.9
20	−1.127	4.7	6.359	1.782	10	−1.099	0.5572	3.0
25	−1.075	4.6	5.446	1.608	9.8	−1.046	0.5416	2.9
30	−1.026	4.5	4.722	1.455	9.2	−0.9975	0.5390	2.8
35	−0.9722	4.3	4.102	1.338	9.0	−0.9415	0.5106	2.7
40	−0.9302	4.1	3.593	1.229	8.4	−0.8984	0.4910	2.5
45	−0.8988	4.0	3.170	1.131	8.2	−0.8661	0.4756	2.5
50	−0.8649	3.7	2.806	1.057	7.8	−0.8299	0.4387	2.3
55	−0.8170	3.6	2.517	0.9851	7.5	−0.7812	0.4259	2.3
60	−0.7566	3.5	2.284	0.9187	7.2	−0.7209	0.4279	2.2
65	−0.7129	3.4	2.067	0.8682	7.2	−0.6756	0.4005	2.2
70	−0.6700	3.4	1.886	0.8183	7.5	−0.6320	0.3905	2.3
75	−0.6304	3.2	1.716	0.7821	7.8	−0.5901	0.3504	2.3
80	−0.5603	3.6	1.608	0.7399	9.2	−0.5212	0.3717	2.7

for the kinematic viscosity of binary solvent mixtures:

$$\begin{aligned}\ln \nu = {} & X_1^3 \ln \nu_1 + 3X_1^2 X_2 \ln \nu_{12} \\ & + 3X_1 X_2^2 \ln \nu_{21} + X_2^3 \ln \nu_2 + R_0,\end{aligned} \tag{3}$$

$$\begin{aligned}R_0 = {} & -\ln\,(X_1 + X_2 M_2/M_1) \\ & + 3X_1^2 X_2 \ln\,(2/3 + M_2/3M_1) \\ & + 3X_1 X_2^2 \ln\,(1/3 + 2M_2/3M_1) \\ & + X_2^3 \ln\,(M_2/M_1),\end{aligned} \tag{4}$$

where M_1, M_2 are the molar masses, and ν_{12}, ν_{21} are fitting parameters valuable by an ordinary least-squares method.[15] The author suggested that Eq. 3 is available only if the ratio of the molecular radii (r_1/r_2) of the two components in the binaries is less than 1.5. In this case, the ratio, reported in the last column of Table 1, is smaller than the imposed limit at all the investigated temperatures. The values of the adjustment parameters ν_{12} and ν_{21}, along with the standard deviations $\sigma(\ln \nu)$ for each isothermal data set, are given in Table 3.

By analyzing a commendably large set of these parameters, it is possible to try some useful considerations about their meaning. Figure 1 shows the trend of the ν_{ij} crossing terms vs. temperature, where the curves represent a fit of the type:

$$\nu_{ij} = C_0 \exp\,(C_1/T), \quad \text{for } (i \neq j) = 1,2 \tag{5}$$

having, in its linear logarithmic form, a correlation coefficient r=0.991 either for ν_{12} and ν_{21}. Physical significance could be attached to these crossing parameters ν_{ij}, being interpreted in terms of quantities related to the specific interactions between components. In fact, in the McAllister hypothesis the formation of three-body aggregates is considered, being represented in an oversimplified picture as {1-1-2}, {2-1-2} for ν_{12}, and {1-2-1}, {1-2-2} for ν_{21} term, where the central unit appears involved in hypothetical ternary aggregates. As the author suggested,[14] other ternary homoaggregated species of the type {1-1-1} or {2-2-2} are neglected having not any importance in the modulation of the adjustable interaction crossing terms.

At this step, it seems reasonable to think that the interaction patterns between 1 or 2 central molecule and the neighboring units in the ternary aggregates are always of the same type, only depending on the chemical nature of the two components. However, their relative intensities should be different in any space direction for different surrounding arrangements. On the basis of these considerations, one may hypothesize that the adjustable crossing parameters in Eq. 3 should have nearly the same statistical weight and therefore they should have a very little different value at any fixed temperature.

For this binary solvent system, McAllister equation provides a set of adjustable parameters very different in magnitude, especially in the low temperature region (see Fig. 1). On the contrary, an increase in the temperature reduces many times these differences.

A more effective measure of these characteristic properties of the crossing terms is provided by the relative differences δ_r obtained from the equation[2)]

$$\delta_r = \frac{|\nu_{12} - \nu_{21}|}{|\nu_{12} - \nu_{21}|_{\max}}. \tag{6}$$

The parameter δ_r is strictly related to the incremental variation of the ν_{ij} parameters and to their point scattering in the variability range. In fact, being $0 \le \delta_r \le 1$ as it has been defined by the Eq. 6 as greater is δ_r as much little is the difference between ν_{ij} values and, as a consequence, the same statistical weight is attributed to the crossing interaction terms between unlike species.

Moreover, working with a large set of data-points, it appears us reasonable to use the average value $\overline{\delta_r}$ in order to check the goodness of the above cited correlation procedure. On these basis, McAllister equation seems to be more effective in describing the viscokinetic properties of these binary mixtures in the high temperature region, while probably it is less efficacious at the lower one. The correlation procedure yields a $\overline{\delta_r}=0.432$, while Eq. 3 reproduces the experimental ν values of Table 1 within $\overline{\Delta\nu}=\pm 0.0533\times 10^{-6}$ m^2 s^{-1}.

Heric Equation. For binary kinematic viscosity data, Heric suggested a suitable equation in the form[16)]

$$\begin{aligned} \ln \nu &= X_1 \ln (\nu_1 M_1) + X_2 \ln (\nu_2 M_2) \\ &\quad - \ln (X_1 M_1 + X_2 M_2) + \Delta_{12}, \end{aligned} \tag{7}$$

$$\Delta_{12} = X_1 X_2 \left[\beta_{12} + \beta_{21}(X_1 - X_2)\right], \tag{8}$$

where β_{ij} are the adjustable coefficients representing the crossing interactions between unlike species. These best-fitting parameters have been computed from the ordinary least squares method[15)] applied to each isothermal set of experimental data of Table 1, and are listed on Table 3 along with the standard deviation $\sigma(\ln \nu)$ at each temperature.

Equation 7 reproduces the experimental values of Table 1 with an average deviation $\overline{\Delta\nu}=\pm 0.0533\times 10^{-6}$ m^2 s^{-1}, being the same uncertainty provided by McAllister equation. From a brief examination, Heric's equation should be preferred to the McAllister one, owing to its simple formula and even if containing the same number of adjustable coefficients.

Figure 2 shows the trend of β_{ij} coefficients vs. temperature and, as one can note, these parameters seem fairly approached at all the investigated temperatures,

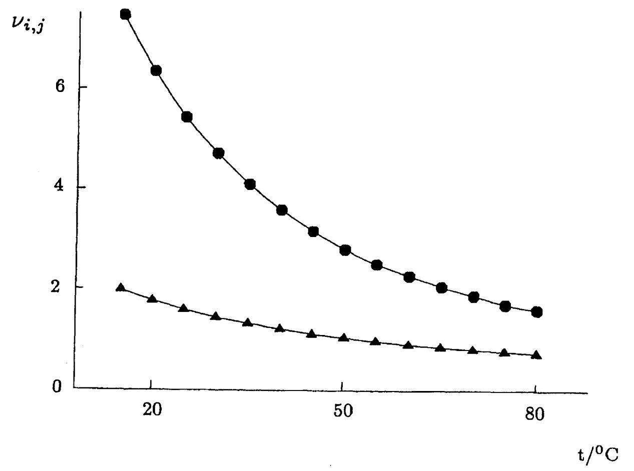

Fig. 1. McAllister's Equation ν_{12} (●) and ν_{21} (▲) parameters vs. temperature.

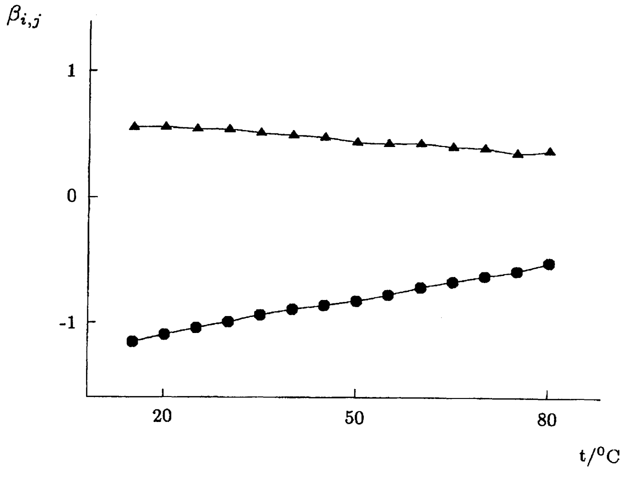

Fig. 2. Heric's Equation β_{12} (●) and β_{21} (▲) parameters vs. temperature.

being the corresponding parameter $\overline{\delta_r}=0.760$.

Auslander Equation. Auslander proposed an equation for best-fitting procedures of viscosity data of the type:[17]

$$X_1(X_1+B_{12}X_2)(\nu-\nu_1)$$
$$+A_{21}X_2(B_{21}X_1+X_2)(\nu-\nu_2)=0, \qquad (9)$$

where A_{21}, B_{12}, B_{21} are three adjustable coefficients, and the other symbols have their usual significance. The fitting parameters obtained by a multilinear regression package TSP are summarized in Table 4, together with the standard deviation $\sigma(\nu)$ at each temperature. The Auslander equation reproduces the experimental ν values of Table 1 within $\overline{\Delta\nu}=\pm 0.0629\times 10^{-6}$ m^2 s^{-1}.

Rational Function. In the literature it has been suggested that rational functions should be more adequate to fit thermomechanical data than that linear polynomials.[18] Thus, starting from King and Queen advices we propose in this paper the following equation for kinematic viscosity:

$$\ln\nu=\frac{X_1(X_1+\gamma_{12}X_2)\ln\nu_1+X_2(X_2+\gamma_{21}X_1)\ln\nu_2}{X_1(X_1+\gamma_{12}X_2)+X_2(X_2+\gamma_{21}X_1)}, \qquad (10)$$

where the γ_{12} and γ_{21} coefficients represent two crossing interaction terms between unlike molecules. The γ_{ij} values are listed in Table 4, together with the average deviation at each temperature. The rational function (Eq. 10) reproduces the experimental values with an average approximation $\overline{\Delta\nu}=\pm 0.0560\times 10^{-6}$ m^2 s^{-1}.

Figure 3 shows the plot of the γ_{ij} vs. temperature. It should be noted that this trend seems to be quite regular, and the average relative difference $\overline{\delta_r}$ is the highest ($\overline{\delta_r}=0.963$) between the corresponding quantities of the others two-parameters fitting procedures considered in this work. In this light, it is possible to attribute the same statistical weight to the two crossing interaction terms between dissimilar species.

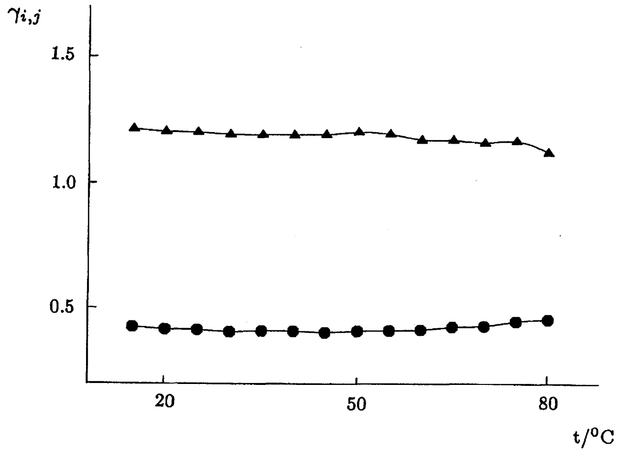

Fig. 3. Rational Equation γ_{12} (●) and γ_{21} (▲) parameters vs. temperature.

Table 4. Coefficients and Standard Deviations of Different Fitting Equations for 1,2-Ethanediol/1,4-Dioxane Solvent System at Various Temperatures

	Auslander				Rational		
t/°C	A_{21}	B_{12}	B_{21}	$10\sigma(\nu)$	γ_{12}	γ_{21}	$10^2\sigma(\ln\nu)$
15	3.531	0.2121	1.365	3.0	0.4268	1.216	2.9
20	3.037	0.1974	1.525	3.1	0.4178	1.206	3.0
25	2.779	0.1931	1.564	2.7	0.4149	1.203	2.9
30	3.101	0.2503	1.260	2.1	0.4072	1.195	2.8
35	2.989	0.2672	1.223	1.8	0.4110	1.194	2.7
40	3.234	0.3240	1.032	1.4	0.4097	1.193	2.5
45	3.273	0.3507	0.9532	1.3	0.4043	1.195	2.5
50	2.835	0.3175	1.097	1.2	0.4099	1.205	2.4
55	2.307	0.2635	1.336	1.2	0.4119	1.197	2.3
60	1.597	0.1784	1.970	1.3	0.4149	1.174	2.1
65	1.031	0.1011	3.098	1.4	0.4263	1.173	2.1
70	0.4197	0.0008	7.632	2.7	0.4298	1.162	2.2
75	0.2106	−0.0337	14.89	3.7	0.4486	1.169	2.3
80	0.1228	−0.0491	25.37	3.8	0.4557	1.123	2.7

Polynomial Equation. The most commonly used fitting equation for experimental data analyses has the form

$$\nu=X_1\nu_1+X_2\nu_2+X_1X_2\sum_{0}^{n}a_n(X_1-X_2)^n, \qquad (11)$$

where a_n are the polynomial coefficients to be evaluated. In this respect, they could represent as many interaction terms between unlike molecules in relation to the selected degree n of the polynomial equation. For comparison purposes, we have obtained a good fit of the experimental ν values by three adjustable coefficients, being selected $n=2$.

The a_n parameters are listed in Table 5, together with the standard deviations at each temperature. Equation 11 reproduces the experimental values of Table 1 within $\overline{\Delta\nu}=\pm 0.0562\times 10^{-6}$ m^2 s^{-1}.

Now, some considerations can be written about the

Table 5. Coefficients a_n and Standard Deviations $\sigma(\nu)$ of Eq. 11 for 1,2-Ethanediol/1,4-Dioxane Solvent System at Various Temperatures

t/°C	a_0	a_1	a_2	$10^2\sigma(\nu)$
15	−33.47	−19.07	−8.433	25
20	−25.81	−13.83	−5.645	22
25	−20.24	−10.33	−4.178	18
30	−16.05	−7.710	−2.869	15
35	−12.83	−5.842	−2.026	12
40	−10.41	−4.500	−1.488	10
45	−8.559	−3.519	−1.103	8.7
50	−7.121	−2.831	−0.8733	7.4
55	−5.894	−2.182	−0.5375	6.2
60	−4.893	−1.617	−0.1081	5.4
65	−4.132	−1.287	−0.0046	4.9
70	−3.495	−0.9883	0.1730	4.6
75	−2.980	−0.8137	0.1749	4.3
80	−2.590	−0.5494	0.3702	4.4

Heric's and this last polynomial function. In fact, Eqs. 7 and 11 could be formally derived by the more general Redlich–Kister one,[19)] being the adjustable coefficients derived from this equation[19)] truncated at different power terms. However, it should be noted that for these binary mixtures, Heric's equation provides better results if compared with polynomial (Eq. 11) one, even if it contains only two adjustable parameters, while the polynomial equation contains three empirical coefficients.

Conclusions

The results of this analysis show that all the selected equations are suitable for the best-fitting viscokinetic data of the ED/DX binary solvent system.

This fact appears not surprising in view of the number of adjustable coefficients in each equation, even if a very large variability of the experimental measurements is observed both with temperature and mixture composition. In this light, it becomes more difficult to suggest any general rule establishing the effectiveness of one fitting procedure over the others.

However, the more suitable comparison between different relations should be restricted to the equations with the same number of adjustable coefficients. Thus, the equation group having two adjustable parameters includes McAllister, Heric, and rational functions. All these fitting procedures applied to the present binary data show a good ability to reproduce experimental values, being comparable the average uncertainties each others.

Nevertheless, the rational function should be preferred owing to the high correlation degree of the fitting parameters. As for the three adjustable coefficients equations is concerned, i.e. Auslander's and polynomial, it should be noted that the treatment of our ED/DX binary data represents a hard test to select the more suitable expression for the best fit of the experimental values. In fact, the reproducibility of the experimental points is about the same obtained by applying the two adjustable coefficient equations. These evidences could suggest the choice of the simplest function containing a reduced number of fitting parameters with respect to the others, being ascertained that these coefficients are related to the specific solvent–cosolvent interactions.

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