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Dynamic Viscosities of *n*-Alkanes and 2-Butanone Mixtures at 20 °C

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Dynamic viscosities, η, of *n*-alkane + 2-butanone mixtures (*n*-alkane = *n*-heptane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, and *n*-hexadecane) have been measured at 20 °C. Deviations from ideality, as defined by $\eta - \eta_{id}$ ($\eta_{id} \propto$ ideal viscosity), are negative in *n*-heptane + 2-butanone, null in *n*-nonane + 2-butanone, and positive in the remaining mixtures, increasing with the number of the carbon atoms of *n*-alkane. Qualitatively, these delvations seem to be related to entropic effects. $\eta - \eta_{id}$ values as calculated from excess volume, V^E, and excess free energy, G^E, data, according to the scheme of Bloomfield and Dewan, agree with experimental ones if absolute rate contributions are neglected.

Introduction

The interactions between the components of a mixed solvent mostly determine both the solubility in it of a polymer and the dimensions of the macromolecular coils in solution (*1*, *2*). *n*-Alkane + 2-butanone mixtures display interesting properties with respect to the solubility of polymers as evidenced by studies on total and preferential sorption equilibria of poly(dimethylsiloxane), PDMS, in those mixtures (*3*-*7*). On the one hand, the homologous series of the *n*-alkanes constitutes the best example of nonpolar liquids to which thermodynamic theories can be properly applied (*8*) and the solvent power for PDMS gradually decreases along the series, going from a very good solvent as *n*-heptane (HEP) to a nonsolvent as the *n*-hexadecane (HED) (*3*-*7*). On the other hand, 2-butanone (MEK) is the first member of the aliphatic ketone series which dissolves PDMS, at 20 °C being a θ solvent (*9*). *n*-Alkane + MEK mixtures provoke MEK autoassociation rupture and readily the mixtures show cosolvent character, i.e., larger solvent power than the pure liquids; the cosolvency increasing with the length of the hydrocarbon chain (*3*-*7*).

In the present paper, measurements of dynamic viscosity, η, at 20 °C for *n*-alkane + MEK mixtures with *n*-alkane = HEP, *n*-nonane (NON), *n*-decane (DEC), *n*-undecane (UND), *n*-dodecane (DOD), and HED are reported. The dynamic viscosity is an integral property of the liquid mixture which has been related to the interactions between liquids (*10*-*12*) and to the structure of the mixture (*11*, *13*, *14*). Our results are first qualitatively analyzed in light of both kinds of effects. Furthermore, a quantitative discussion is undertaken on grounds of the two major semiempirical theories of liquid viscosity, namely, the absolute rate and free volume theories following the theoretical scheme developed by Bloomfield and Dewan (*11*).

Experimental Section

All the organic liquids used in this study were of Merck origin and had nominal purities of 99.5% (MEK) and 99.0% (*n*-alkanes). The binary liquid mixtures were prepared by weighing the individual components with an accuracy of ±0.0001 g. The viscosities of the pure liquids and their mixtures were measured with two modified Ubbelohde viscometers, calibrated with benzene, doubly distilled water, and aqueous solutions of sucrose. Flow times were repeatedly determined, the standard

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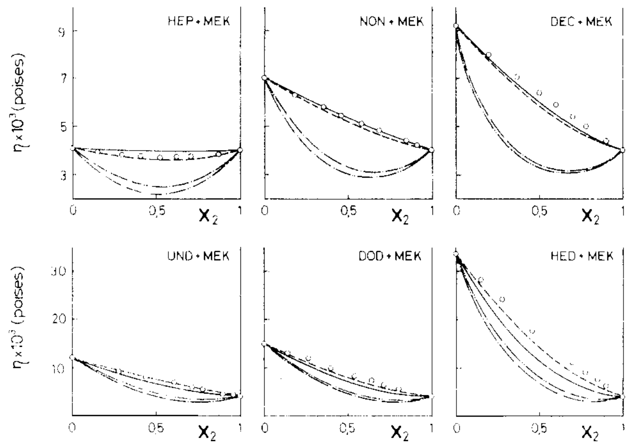

Figure 1. Dependences on mixture composition (x_2) of experimental viscosities (O) and viscosities calculated through the Bloomfield and Dewan formalism (in cP) at 20 °C for n-alkane + MEK mixtures, n-alkane = HEP, NON, DEC, UND, DOD, and HED: —, η_{id}; - - -, $\eta_{id}\eta_{fv}$; -·-·, $\eta_{id}\eta_{ar}$; -··-··, $\eta_{id}\eta_{fvcar}$.

deviations being within ±0.05 s. Temperature of the viscometer was maintained at 20.00 ± 0.02 °C by a water bath. The required density values have been reported earlier (*15*). The viscosity values were estimated to be precise to 0.3%.

Results and Discussion

In Table I, dynamic viscosities (in cP), η, for the diverse n-alkane + MEK systems are gathered together with the viscosities for the ideal mixtures (η_{id}) defined by Arrhenius as

$$\ln \eta_{id} = x_1 \ln \eta_1 + x_2 \ln \eta_2$$

x_i standing for molar fraction of component i. The comparison between experimental and ideal viscosities is graphically shown in Figure 1 vs. system composition. Deviation from ideality ($\eta - \eta_{id}$) is negative in HEP + MEK, null in NON + MEK and positive in the remaining systems increasing with the number of carbon atoms of the hydrocarbon (n).

Qualitatively, the departures from ideality of dynamic viscosities of mixtures have been related to their excess properties through considerations on the structure of the mixture and the interactions between mixture components (*10*, *14*). Thus, whereas both pure liquids display ordered structures, due in MEK to the strong dipole of the carbonyl group and in n-alkane to autoassociations through correlations between chains, in their mixtures those orders are destroyed and would yield positive V^E (excess volume) and S^E (excess entropy of mixing) values, both increasing with n-alkane length. Interactions between CO groups and methyl and methylene groups of n-alkanes are also operative in these systems and they are the dipole-induced dipole type. This effect would produce an increase on V_E and on H^E (excess enthalpy) proportional to the methylene units in n-alkane. Likewise, the differences in molecular sizes between the mixture components must lead to interstitial accommodation of MEK molecules in the mixture and hence to a negative contribution to V^E. A further effect to consider is the difference in free volume between MEK and n-alkanes. It would contribute negatively to S^E, its contribution increasing in magnitude with n. Moreover, conformational rearrangements are possible in longer n-alkanes, and these will also contribute negatively to S^E (*15*).

Diverse correlations between $\Delta\eta$ and the excess properties have been found (*10*, *14*). Thus, in mixtures with strong interactions between both components (negative H^E and G^E, excess free energy of mixing) $\Delta\eta$ ($\eta - \eta_{id}$) values have been found to be positive (*12*, *13*, *16*), whereas in those with no specific interactions (positive H^E and G^E) $\Delta\eta$'s should be negative (*17*). Likewise, the sign of $\Delta\eta$ has also been found to be correlated with that of V^E, the sign of both magnitudes being opposite (*10*, *13*). In n-alkane + MEK systems both H^E and V^E are positive and increase with n whereas G^E is also positive and practically does not depend on n (*15*). Therefore, negative $\Delta\eta$ values would be expected for n-alkane + MEK mixtures, with alkanes of higher n giving increasingly negative values of $\Delta\eta$. Instead, $\Delta\eta$ was found to increase with n, becoming less negative and changing sign at n = 9, the same alkyl chain length at which conformational rearrangements start to take

Table I. Experimental, η, and Ideal, η_{id}, Viscosities (cP) of n-Alkane + MEK Mixtures at 20 °C at Different MEK Mole Fraction Composition, x_2

x_2	η	η_{id}
	HEP + MEK	
0.0000	0.409	
0.1550	0.309	0.407
0.2921	0.382	0.405
0.4143	0.378	0.404
0.5238	0.376	0.402
0.6227	0.380	0.401
0.7123	0.375	0.400
0.8684	0.383	0.398
1.0000	0.396	
	NON + MEK	
0.0000	0.711	
0.1811	0.633	0.640
0.3322	0.582	0.586
0.4603	0.543	0.543
0.5702	0.511	0.510
0.6655	0.485	0.482
0.8279	0.439	0.438
0.8919	0.422	0.419
1.0000	0.396	
	DEC + MEK	
0.0000	0.920	
0.2012	0.803	0.777
0.3617	0.711	0.679
0.4927	0.644	0.608
0.6018	0.588	0.554
0.6939	0.541	0.513
0.7727	0.502	0.480
0.9007	0.438	0.431
1.0000	0.396	
	UND + MEK	
0.0000	1.179	
0.2923	0.891	0.857
0.4382	0.779	0.731
0.5575	0.691	0.642
0.7006	0.591	0.550
0.7783	0.541	0.505
0.9035	0.454	0.405
0.9547	0.422	0.417
1.0000	0.396	
	DOD + MEK	
0.0000	1.450	
0.1235	1.318	1.235
0.2292	1.191	1.077
0.4008	0.983	0.863
0.5342	0.835	0.725
0.6408	0.739	0.632
0.7280	0.632	0.564
0.8006	0.563	0.514
1.0000	0.396	
	HED + MEK	
0.0000	3.340	
0.1556	2.855	2.397
2.2800	2.415	1.839
0.4667	1.730	1.235
0.7000	1.084	0.751
0.7778	0.880	0.637
0.8400	0.731	0.558
0.8909	0.613	0.500
1.0000	0.396	

place as shown by different techniques (*18*, *19*). On the other hand, S^E values in n-alkane + MEK mixtures are positive and largely increase as n grows (*15*). As a conclusion from this hurried qualitative analysis, it seems then, those large S^E values are mainly responsible for the positive values found for $\Delta\eta$.

On the other hand, η deviations from ideality may be quantitatively related to the thermodynamic properties of mixtures through the two major semiempirical theories of liquid viscosity, namely, the absolute rate and free volume theories. According to Bloomfield and Dewan (BD) scheme (*11*) η/η_{id} is evaluated by

$$\ln(\eta/\eta_{id}) = \alpha \ln \eta_{fv} + \beta \ln \eta_{ar} \qquad (1)$$

where η_{fv} and η_{ar} represent the deviations from ideal behavior calculated by the free volume and absolute rate reaction theories, respectively, and α and β are weighting coefficients, which usually are made equal to 1. Both contributions to the departure from ideality are respectively given by

$$\ln \eta_{fv} = 1/(\tilde{v} - 1) - x_1/(\tilde{v}_1 - 1) - x_2/(\tilde{v}_2 - 1) \qquad (2)$$

$$\ln \eta_{ar} = -\Delta G^R/RT \qquad (3)$$

where G^R is the residual free energy on mixing. In the BD scheme the relationships between η_{fv} and η_{ar} and the excess properties of mixtures is made through the statistical thermodynamic theory of liquid mixtures proposed by Flory and coworkers (*20*–*22*). Thus, $\tilde{v}$ is defined by $\tilde{v} = V/V^*$, V and V^* being molar and molar hard-core volumes, respectively. $\tilde{v}$ is related to V^E by

$$\tilde{v} = V^E/(x_1V_1^* + x_2V_2^*) + \Psi_1\tilde{v}_1 + \Psi_2\tilde{v}_2 \qquad (4)$$

whereas G^R is related to G^E by

$$G^R = G^E + RT\{x_1 \ln(x_1/\Psi_1) + x_2 \ln(x_2/\Psi_2)\} \qquad (5)$$

with Ψ_i, the segment fraction of component i, given by

$$\Psi_i = x_iV_i^*/(x_1V_1^* + x_2V_2^*) \qquad (6)$$

In Figure 1, η as calculated from eq 1–3, with $\alpha = 1$ and $\beta = 0$, with $\alpha = 0$ and $\beta = 1$ and finally with $\alpha = 1$ and $\beta = 1$ are represented vs. system composition and compared to experimental values. The data needed for these calculations are core volumes V_i^* in cm^3 mol^{-1} (*20*, *23*), 68.87 (MEK), 113.65 (HEP), 142.00 (NON), 156.10 (DEC), 170.30 (UND), 184.30 (DOD), and 241.10 (HED), and reduced volumes $\tilde{v}_i$, 1.3004 (MEK), 1.2886 (HEP), 1.2587 (NON), 1.2485 (DEC), 1.2402 (UND), 1.2336 (DOD), and 1.2144 (HED) (*20*, *23*) and G^E and V^E are from ref (*15*).

As can be seen in Figure 1, η values do not agree with experimental ones when $\alpha = 0$ and $\beta = 1$, i.e., when deviations from ideality are solely defined by η_{ar} contribution, probably due to the large G^E values and to the large molecular volume differences between mixture components, whereas deviations from ideality are well explained through the free volume theory, $\alpha = 1$ and $\beta = 0$. An increase in free volume allows the hydrocarbon long chains to adopt a greater number of configurations and therefore to increase the configurational entropy, which seems to be the agent causing the departure from ideal behavior, in accordance with the qualitative conclusion arrived at before.

Glossary

η	dynamic viscosity
n	number of carbon atoms
η_{id}	dynamic viscosity for ideal mixtures
V^E	excess volume
G^E	excess free energy of mixing
x_i	molar fraction of component i
S^E	excess entropy of mixing
H^E	excess enthalpy of mixing
$\Delta\eta$	difference between experimental and ideal η's
fv (subscript)	from free volume theory
ar (subscript)	from absolute rate reaction theory
G^R	residual free energy
$\tilde{v}$	reduced volume
V	molar volume
V^*	hard-core volume
Ψ	segment fraction

Registry No. MEK, 78-93-3; HEP, 142-82-5; NON, 111-84-2; DEC, 124-18-5; UND, 1120-21-4; DOD, 112-40-3; HED, 544-76-3.

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