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Dynamic Viscosity of Multicomponent Liquid Mixtures

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In an effort to develop and test predictive models for the dynamic viscosity of multicomponent liquid mixtures, some pertinent experimental data are reported in this work. The densities and kinematic viscosities of the quaternary system benzene + cyclohexane + ethanol + *n*-heptane and its constituent binaries have been measured at 298.15 K. These data and literature data for a number of multicomponent liquid mixtures have been used for testing the predictive character of the generalized corresponding states (GCS) model of Teja and Rice, as modified recently. The model requires binary information in order to predict the behavior of multicomponent mixtures. Binary parameters of the model for 24 binary mixtures are reported. The performance of the model is satisfactory.

Introduction

Process fluids in chemical industries are, generally, multicomponent mixtures, and thus, knowledge of their thermophysical properties is of importance for a rational chemical process design. It is impractical to measure all thermophysical properties at all external conditions in multicomponent systems. In this respect, simple models, which need a limited amount of experimental information in order to predict with acceptable accuracy the behavior of multicomponent mixtures, are of considerable value. It should be pointed out that essential testing of these models requires consistent experimental data for the viscosities of pure liquids, of their binaries, and of their multicomponent mixtures. In a recent work (*1*), we applied successfully the generalized corresponding states (GCS) model of Teja and Rice (*2*), with new mixing rules for the pseudocritical temperature of the binary mixtures, to the prediction of the dynamic viscosity of two ternary systems measured in this laboratory. The GCS model requires binary information in order to predict the viscosity of multicomponent mixtures. The objective of this work is to make an extensive test of the GCS model against experimental data for various types of ternary systems, including highly nonideal systems. In addition, experimental data for a quaternary system are provided and used for further testing of the GCS model. Literature data for a number of binary systems, along with our own experimental data for three binary systems, are used for extracting the necessary information for the prediction of the dynamic viscosity of the multicomponent systems.

Experimental Section

Materials. All pure liquids used in this work were pro analysi grades from Merck, except for cyclohexane, which was puriss. grade from Fluka. Their purity was determined by gas–liquid chromatography and was better than 99.7% for benzene, better than 99.5% for cyclohexane, better than 99.5% for ethanol, and better than 99.0% for *n*-heptane. The liquids were used as received without any further purification. Pure-component properties are shown in Table I. The mixtures were prepared by weight with a precision of ±0.0001 g. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions.

Table I. Properties of Pure Liquids at 298.15 K

liquid	ρ, g/cm^3 exptl	ρ, g/cm^3 lit.	η, cP exptl	η, cP lit.
benzene	0.8735	0.8737[a]	0.6048	0.6028,[b] 0.606[c]
cyclohexane	0.7738	0.7739[d]	0.8984	0.8980[a]
ethanol	0.7851	0.7852[e]	1.0832	1.0812[e]
n-heptane	0.6796	0.6810,[f] 0.680[g]	0.3870	0.386,[b] 0.3967[h]

[a] Reference 3. [b] Reference 4. [c] Reference 5. [d] Reference 6. [e] Reference 7. [f] Reference 8. [g] Reference 9. [h] Reference 10.

Table II. Dynamic Viscosities and Densities of the System Cyclohexane (1)–Benzene (2) at 298.15 K

x_1	ρ, g/cm^3	η_{exp}, cP	η^{ID}, cP	η_{calc}, cP
0.0984	0.8597	0.582	0.624	0.584
0.1986	0.8467	0.576	0.650	0.577
0.3009	0.8345	0.579	0.677	0.578
0.4008	0.8235	0.589	0.705	0.589
0.4989	0.8135	0.609	0.734	0.608
0.5520	0.8084	0.623	0.750	0.623
0.6007	0.8039	0.639	0.764	0.639
0.6478	0.7998	0.653	0.779	0.657
0.7475	0.7916	0.699	0.811	0.705
0.8011	0.7874	0.733	0.820	0.736
0.9022	0.7800	0.803	0.863	0.809

Table III. Dynamic Viscosities and Densities of the System Cyclohexane (1)–Ethanol (2) at 298.15 K

x_1	ρ, g/cm^3	η_{exp}, cP	η^{ID}, cP	η_{calc}, cP
0.0999	0.7805	1.003	1.062	1.017
0.1993	0.7769	0.951	1.042	0.966
0.2995	0.7751	0.923	1.023	0.925
0.3987	0.7734	0.892	1.004	0.892
0.5003	0.7727	0.872	0.985	0.866
0.5500	0.7725	0.861	0.979	0.855
0.6011	0.7721	0.851	0.967	0.845
0.7014	0.7719	0.831	0.949	0.832
0.8030	0.7719	0.826	0.931	0.827
0.9006	0.7723	0.840	0.914	0.839

Density. A vibrating-tube densitometer of Anton Paar Model DMA 60/602 was used for measuring the liquid densities ρ. Bidistilled water and air were used as calibrating substances. The temperature in the measuring cell was regulated to 25.00 ± 0.01 °C through a Haake ultrathermostat and measured by a precision digital thermometer of Systemteknik Model S1220 with a specially designed sensor. The estimated error in the density is $\pm 5 \times 10^{-6}$ g/cm^3.

Viscosity. The kinematic viscosities ν of pure liquids and their mixtures have been measured with two Ubbelohde viscometers, which were thoroughly cleansed, dried, and calibrated in each case. The precision in efflux time was 0.1 s. Viscosity measurements were conducted in a precision thermostat, Model TAMSON TMV70, microprocessor controlled with a temperature stability better than ±0.01 °C. The estimated error in the dynamic viscosity η ($\eta = \nu\rho$) is ±0.0015 cP.

Experimental dynamic viscosities and densities for the binary systems containing cyclohexane are reported in Tables II–IV. Corresponding experimental data for the quaternary system

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Table IV. Dynamic Viscosities and Densities of the System Heptane (1)–Cyclohexane (2) at 298.15 K

x_1	ρ, g/cm^3	η_{exp}, cP	η^{ID}, cP	η_{calc}, cP
0.1008	0.7602	0.776	0.824	0.770
0.2001	0.7488	0.680	0.760	0.683
0.2493	0.7427	0.641	0.728	0.643
0.3511	0.7319	0.578	0.668	0.581
0.4012	0.7272	0.556	0.643	0.560
0.4993	0.7178	0.520	0.589	0.517
0.5726	0.7117	0.483	0.557	0.489
0.6007	0.7089	0.479	0.541	0.483
0.7471	0.6972	0.447	0.478	0.442
0.8984	0.6862	0.409	0.421	0.408

Table V. Dynamic Viscosities and Densities of the System Ethanol (1)–Benzene (2)–Heptane (3)–Cyclohexane (4) at 298.15 K

x_1	x_2	x_3	ρ, g/cm^3	η_{exp}, cP	η^{ID}, cP	η_{calc}, cP
0.1607	0.4255	0.0643	0.7992	0.556	0.738	0.571
0.1743	0.4579	0.2761	0.7723	0.458	0.611	0.468
0.5657	0.0925	0.1130	0.7642	0.701	0.874	0.720
0.4452	0.1949	0.1192	0.7726	0.622	0.816	0.650
0.3115	0.3094	0.1258	0.7812	0.560	0.755	0.586
0.1630	0.4359	0.1321	0.7900	0.518	0.695	0.531
0.5551	0.0906	0.0533	0.7734	0.746	0.916	0.769
0.4365	0.1894	0.0582	0.7817	0.667	0.859	0.695
0.3045	0.3021	0.0612	0.7905	0.602	0.799	0.627
0.3273	0.3236	0.2631	0.7631	0.494	0.671	0.517
0.4666	0.2033	0.2477	0.7548	0.556	0.732	0.574
0.5907	0.0959	0.2356	0.7463	0.624	0.791	0.635
0.1670	0.4468	0.2039	0.7809	0.488	0.651	0.497
0.3187	0.3165	0.1924	0.7722	0.523	0.713	0.550
0.5769	0.0952	0.1725	0.7554	0.658	0.832	0.676
0.2977	0.5837	0.0584	0.8228	0.555	0.714	0.573
0.4734	0.4000	0.0540	0.8099	0.622	0.797	0.644
0.5818	0.2975	0.0518	0.8013	0.683	0.850	0.700
0.7272	0.1587	0.0487	0.7883	0.784	0.926	0.796
0.3176	0.0515	0.0303	0.7715	0.750	0.909	0.768
0.0929	0.0585	0.1469	0.7566	0.639	0.788	0.656
0.0864	0.2270	0.0331	0.7846	0.655	0.810	0.659
0.1708	0.1132	0.0677	0.7708	0.671	0.836	0.687
0.2023	0.1302	0.5608	0.7151	0.439	0.551	0.444
0.1084	0.0666	0.5955	0.7101	0.435	0.540	0.447
0.3704	0.0598	0.5197	0.7114	0.466	0.606	0.486
0.1052	0.2679	0.5708	0.7246	0.404	0.508	0.408
0.8156	0.0758	0.0462	0.7796	0.860	0.975	0.869
0.8142	0.0372	0.0230	0.7782	0.906	1.009	0.918
0.8360	0.0372	0.0947	0.7649	0.837	0.954	0.838
0.8002	0.1475	0.0227	0.7955	0.855	0.963	0.859
0.1530	0.7029	0.0612	0.8313	0.528	0.661	0.539
0.0808	0.7458	0.1295	0.8213	0.491	0.605	0.496
0.2833	0.6513	0.0275	0.8389	0.571	0.711	0.586
0.0795	0.7210	0.0308	0.8351	0.543	0.664	0.549

ethanol–benzene–*n*-heptane–cyclohexane are reported in Table V.

GCS Method for Viscosity

A detailed presentation of the GCS method may be found in the original publication of Teja and Rice (*2*) and in our previous work (*1*). In the present work we will confine ourselves to the essentials of the method. The GCS equation for the dynamic viscosity of a fluid with critical constants T_c, P_c, and V_c and molecular weight M is

$$\ln(\eta\xi) = \ln(\eta\xi)^{r1} + \frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}[\ln(\eta\xi)^{r2} - \ln(\eta\xi)^{r1}] \qquad (1)$$

where ω is the acentric factor and

$$\xi = V_c^{2/3} T_c^{-1/3} M^{-1/3} \qquad (2)$$

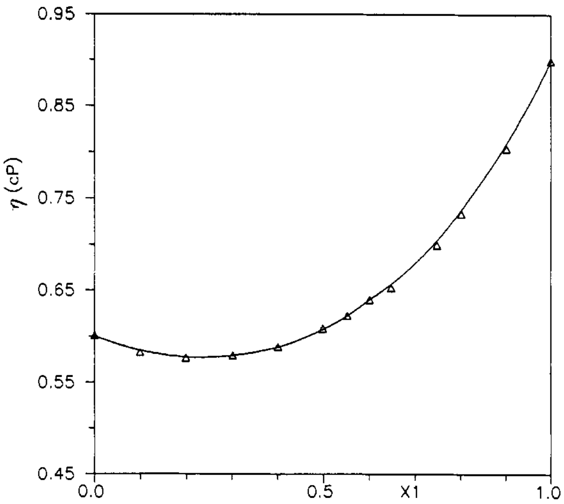

Figure 1. Dynamic viscosities of the cyclohexane (1) + benzene (2) mixture at 25 °C. Solid line was calculated by the GCS method.

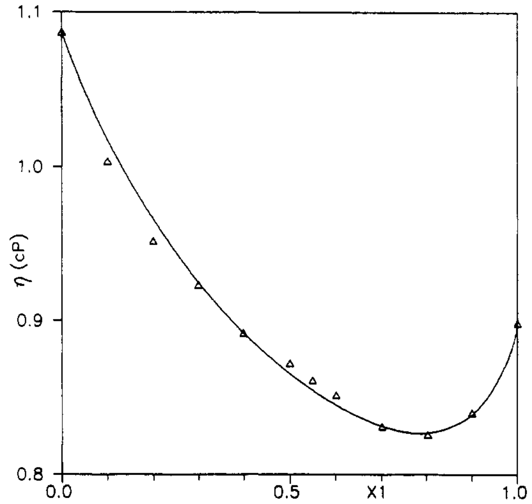

Figure 2. Dynamic viscosities of the cyclohexane (1) + ethanol (2) mixture at 25 °C. Solid line was calculated by the GCS method.

The choice of the reference fluids indicated by superscripts r1 and r2 is in essence arbitrary. The following combining and mixing rules have been proposed for the mixtures (subscript m).

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \qquad (3)$$

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \qquad (4)$$

$$\omega_m = \sum_i x_i \omega_i \qquad (5)$$

$$M_m = \sum_i x_i M_i \qquad (6)$$

$$V = ((V_{cii}^{1/3} + V_{cjj}^{1/3})/2)^3 \qquad (7)$$

$$T_{cij} V_{cij} = \psi_{ij}(T_{cii} V_{cii} T_{cjj} V_{cjj})^{0.5} \qquad (8)$$

x_i is the mole fraction of component i in the mixture. ψ_{ij} in eq 8 is a binary interaction coefficient that must be calculated from experimental data. Seeking an improvement of the performance of the GCS method for highly nonideal systems, the following van Laar type mixing rule has been proposed for ψ_{ij} (*1*)

$$\psi_{ij} = 1 - \frac{K_{ij} K_{ji}}{x_i' K_{ij} + x_j' K_{ji}} \qquad (9)$$

where

$$x_i' = \frac{x_i}{x_i + x_j} \qquad (10)$$

When $K_{ij} = K_{ji}$, ψ_{ij} is, as originally reported (*2*), independent of composition.

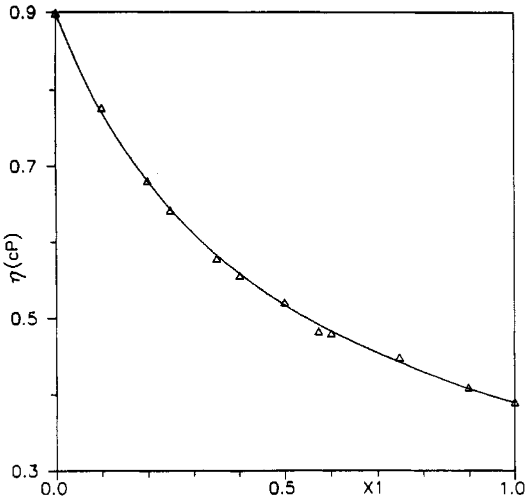

Figure 3. Dynamic viscosities of the *n*-heptane (1) + cyclohexane (2) mixture at 25 °C. Solid line was calculated by the GCS method.

Table VI. Binary Parameters for Some Representative Systems

system	T, K	K_{12}	K_{21}	ref	AAD, %
ethanol–propanol	303.15	–0.0082	–0.0085	1	0.30
methanol–propanol	303.15	–0.0348	–0.0425	1	0.33
methanol–ethanol	283.15	–0.0046	–0.0037	1	0.33
methanol–ethanol	293.15	–0.0146	–0.0090	1	0.47
methanol–ethanol	303.15	–0.0206	–0.0098	1	0.69
methanol–ethanol	313.15	–0.0251	–0.0108	1	0.63
methanol–ethanol	323.15	–0.0190	–0.0111	1	0.33
ethanol–2-propanol	298.15	–0.0069	–0.0074	4	0.23
acetone–ethanol	298.15	0.1154	0.1450	4	0.66
acetone–methanol	298.15	0.0588	0.1217	4	0.18
acetone–isooctane	298.15	–0.0148	–0.0123	3	0.80
cyclohexane–2-propanol	298.15	0.0702	0.1988	4	0.62
carbon tetrachloride–2-propanol	298.15	0.0769	0.2474	4	0.37
carbon tetrachloride–cyclohexane	298.15	0.0227	0.0299	4	0.14
chloroform–methanol	298.15	–0.1590	–0.0163	4	2.18
chloroform–ethanol	298.15	–0.0614	–0.0598		0.25
acetone–toluene	298.15	–0.0143	–0.0078	3	0.33
isooctane–toluene	298.15	0.0384	0.0345	3	0.18
methanol–water	283.15	–0.4441	–0.3069	1	2.04
methanol–water	293.15	–0.4101	–0.2902	1	1.66
methanol–water	303.15	–0.3640	–0.3050	1	1.44
methanol–water	313.15	–0.3374	–0.3008	1	1.62
methanol–water	323.15	–0.3148	–0.3068	1	1.03
ethanol–water	283.15	–0.7108	–0.2574	1	2.85
ethanol–water	293.15	–0.6289	–0.2510	1	2.43
ethanol–water	303.15	–0.5294	–0.2465	1	2.48
ethanol–water	313.15	–0.5014	–0.2350	1	2.13
ethanol–water	323.15	–0.4690	–0.2262	1	1.86
propanol–water	303.15	–0.5768	–0.2110	1	2.44
ethanol–benzene	298.15	0.2148	0.0544	2	0.75
heptane–cyclohexane	298.15	0.0525	0.0370	2	0.62
heptane–benzene	298.15	0.0853	0.0618	2	0.59
cyclohexane–ethanol	298.15	0.0265	0.1860	2	0.49
cyclohexane–benzene	298.15	0.0800	0.0700	2	0.74
ethanol–heptane	298.15	0.3710	0.0435	2	0.90

Table VII. Prediction of Viscosity of Some Representative Ternary Systems by the CCS Model

system	T, K	exptl data	AAD, %
methanol–ethanol–water	283.15	11	8.87
	293.15	11	6.74
	303.15	11	4.91
	313.15	11	4.49
	323.15	11	8.06
methanol–propanol–water	303.15	11	8.19
ethanol–propanol–water	303.15	11	10.73
methanol–ethanol–propanol	303.15	11	0.34
ethanol–cyclohexane–2-propanol	298.15	7	2.10
chloroform–ethanol–methanol	298.15	7	4.42
carbon tetrachloride–cyclohexane–2-propanol	298.15	7	4.56
acetone–isooctane–toluene	298.15	12	0.57
ethanol–benzene–heptane	298.15	12	1.97

In Figures 1–3 are shown the experimental viscosity data for the binary mixtures containing cyclohexane. The solid curves in these figures were calculated by the GCS method. Densities and viscosities for the binaries ethanol + *n*-heptane, ethanol + benzene, and benzene + *n*-heptane have been measured previously (*1*). The binary GCS parameters for 24 binary mixtures are reported in Table VI, along with the average absolute deviation (AAD) of fit. Comparison of this table with the corresponding table of ref 2 shows that the use of the van Laar type mixing rule used in the present work leads to a significant improvement of the GCS method. As observed in Table VI, K_{ij} values depend significantly on temperature. Use, for instance, of the K_{ij} values obtained at 20 °C to higher or lower temperatures leads to the average absolute deviations indicated in parentheses in Table VI. The parameters of this table have been used for the prediction of ternary and quaternary viscosities. In Table VII are shown the average absolute deviations between experimental and predicted viscosities for a number of representative ternary systems. In Table V are shown the predicted viscosities of our quaternary system on the basis of the binary parameters of Table VI. In the quaternary system the calculations have been performed by treating it as a pseudobinary system, the one pseudocomponent being the binary ethanol + benzene and the other being the binary heptane + cyclohexane. The two pseudocomponents were used also as the reference fluids. The average absolute deviation for the quaternary system is 2.40%, which is very low in view of the highly nonideal character of this system. For the same system the maximum deviation between experimental and calculated viscosities is 5.04%. Also in the Table V are shown the calculated viscosities when the system is considered ideal, namely

$$\ln \eta^{\mathrm{ID}} = \sum_i x_i \ln \eta_i \tag{11}$$

Ideal viscosities are also reported in Tables II–IV, along with the calculated viscosities. From these values one can appreciate, on the other hand, the departure from ideal behavior of our systems and, on the other hand, the performance of the GCS model.

In conclusion, the GCS method is a promising tool not only for correlated viscosity data but also for predicting with reasonable accuracy the viscosity of multicomponent mixtures.

List of Symbols

K_{ij}	binary interaction coefficient
M	molar mass
T	absolute temperature
V	volume
x	mole fraction

Greek Letters

η	dynamic viscosity
ν	kinematic viscosity
ξ	quantity defined by eq 2
ρ	density
ψ	binary coefficient
ω	accentric factor

Subscripts

c	critical constant
i	quantity pertinent to component i
ij	quantity pertinent to pair ij

m	mixture quantity

Superscripts

ID	ideal mixture
ri	reference fluid *i*

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Physical Behavior of Some Reaction Media. Density, Viscosity, Dielectric Constant, and Refractive Index Changes of Ethanol–Cyclohexane Mixtures at Several Temperatures

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Viscosities, densities, dielectric constants, and refractive indexes were determined for ethanol–cyclohexane mixtures at 15, 20, 25, 30, 35 °C and over the whole composition range. These properties are represented by means of empirical relations wherein the composition and temperature effects are involved. These equations fit the experimental data with an uncertainty of the same order of magnitude with the corresponding experimental error. The analysis of data evidences the occurrence of changes in the self-association of ethanol with changing composition.

Introduction

This paper is a part of continuing research on the kinetics of S_N2 reactions between ions and dipolar molecules in solvents where the ionic reactant associates to form ion pairs (*1*–*4*).

In previous papers we studied the kinetics of the reaction of sodium ethoxide and methyl iodide in ethanol–dioxane solvent systems (*3*), where the mixture of two organic solvents, in various proportions, enabled us to change the physical properties of the reaction media. In these investigations, in agreement with analogous literature data (*5*), we observed that the corresponding reactions are markedly accelerated as the dielectric constant of the medium is progressively decreased. This effect has been explained by assuming that the nonelectrostatic solute–solvent interactions are more important than the electrostatic ones. Thus, we assumed that the reactant-solvating ability of the medium is changed by the formation of a polar complex between dioxane and ethanol; the formation of such a complex has been detected in previous investigations (*6*).

In an attempt to supply further evidence for this assumption, we decided to extend our kinetic studies to binary ethanol–cyclohexane solvent systems, where the possibility of formation of polar associates through hydrogen bonds does not exist.

However, one problem, generally encountered in such studies, is to correlate reaction rate data with the physical properties of the corresponding media. It should be noted that, among the many intensive physical properties of liquids, the dielectric constant (ϵ), the viscosity (η), and the index of refraction (n) remain the common solvent parameters used to interpret medium effects upon mechanisms of reactions for polar and ionic species, as well as upon electrochemical data and ionic equilibria (*7*–*9*).

Although extensive tabulation of values of these properties for pure solvents are generally available, literature data for various binary solvent systems are often incomplete and may be reported only as empirical graphs.

This situation has encouraged us to make a series of systematic measurements of density, viscosity, dielectric constant, and refractive index of ethanol–cyclohexane mixtures over the whole composition range and temperatures from 15 to 35 °C. An attempt has been made to express these properties by means of single equations, wherein the temperature and composition effects are involved. Some physical properties of the above-mentioned binary mixtures have been previously reported in the literature (*10*–*14*). However, these studies have been made at very different composition or temperature ranges than those used in our kinetic experiments.

Experimental Section

Reagents. Absolute ethanol (Fluka, p.a.) was further purified according to a recommended method (*15*).

Cyclohexane (Merck GR > 99.5%, bp = 80.7°/760 mmHg) was refluxed and then fractionally redistilled. In all distillations only the middle fraction coming over at the reported boiling point and comprising about 75% was retained. Pure-component physical properties were measured and compared to average literature data to assure that there were no significant effects due to impurities (Table I). Mixtures were gravimetrically prepared on a Mettler analytical balance just before their use. The probable error in the cyclohexane mole fraction X_2 is estimated to be less than 0.0001.

Measurements. The apparatus and procedure for the experimental measurements of density, viscosity, and dielectric constant were identical with those described previously (*6*).

Refractive index measurements were carried out by means of a thermostated Abbe refractometer (Jena). Values were

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