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Transport properties of binary liquid mixtures – Candidate solvents for optimized flue gas cleaning processes

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Abstract: Thermal conductivities and viscosities of three pure chemicals, monoethanolamine (MEA), tetraethylene glycol dimethyl ether (TEGDME) and polyethylene glycol 200 (PEG 200) and two binary mixtures (MEA+TEGDME and MEA+PEG 200) were measured at six temperatures: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K and atmospheric pressure. Measurement of the thermal conductivities was based on a transient hot wire measurement setup, while the viscosities were measured with a digital Stabinger SVM 3000/G2 viscometer. From these data, deviations in the thermal conductivity and viscosity were calculated and fitted to the Redlich–Kister equation. Thermal conductivities of mixtures were correlated using the Filippov, Jamieson, Baroncini and Rowley models, while the viscosity data were correlated with the Eyring-UNIQUAC, Eyring-NRTL and McAlister models.

Keywords: thermal conductivity; viscosity; modelling; MEA; TEGDME; PEG 200.

INTRODUCTION

Modelling and simulation of industrial processes in thermal power plants, as well as the design of appropriate facilities for treating flue gas, require the thermophysical properties of the applied solvent as input data. Among other properties, it is necessary to know the thermal conductivity and viscosity of the used solvent in the range of working temperature of the plant. Multitudes of studies have been conducted in the past years in the quest for the most suitable solvent for the removal of carbon dioxide.^{1–6} Numerous industrial plants, some of which have been in operation for over forty years, emerged from these studies.

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Primary amines exhibit the highest level of carbon dioxide binding. For many years, primary alkanolamines, monoethanolamine (MEA) in the first place, were successfully used as chemical solvents in industrial plants. However, corrosion processes, which intensify with increasing solvent concentration, must also be taken into account in thermal power plants. Secondary amines show slightly weaker level of binding of carbon dioxide, and this degree is further reduced with tertiary amines. However, secondary and tertiary amines exhibit better affinity for the binding of sulphur dioxide, another toxic greenhouse gas (general considerations related to the environmental impact of the industrial gases are presented in Supplementary material to this paper). Choice of the most suitable solvent will be affected by associated energy costs of regeneration: since the recovery of the solvent is mainly done through thermal regeneration, a compromise is made between binding affinity and ability to regenerate the solvent. Tetraethylene glycol dimethyl ether (TEGDME) is a polar aprotic solvent that has already found commercial application in a regenerative process for SO₂ removal.⁷ Polyethylene glycols (PEG) are important industrial solvents of low toxicity, low vapour pressure, high chemical stability and low melting points. The high solubility of SO₂ and relatively easy desorption are the main advantages of polyethylene glycol 200 (PEG 200), which reduces power consumption in the solvent regeneration process.⁸ Thanks to these characteristics, it could be used in the purification of flue gases from power plants. Unlike MEA, both TEGDME and PEG 200 are physical solvents which means that absorption process occurs without chemical reaction. Investigations^{9,10} have shown that mixtures of physical and chemical solvents often show better characteristics regarding binding capacity and selectivity than aqueous solutions of alkanolamines, traditionally used in gas purification processes.

In this work, experimental thermal conductivities and viscosities are reported for three pure substances, MEA, TEGDME and PEG 200, and two binary mixtures, MEA+TEGDME and MEA+PEG 200, at six temperatures, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 K and atmospheric pressure. From these experimental data, deviations in thermal conductivity ($\Delta\lambda$) and viscosity ($\Delta\eta$) were calculated and correlated by the Redlich–Kister equation.¹¹ For correlating the thermal conductivities of the mixtures, the Filippov,¹² Jamieson,¹³ Baroncini¹⁴ and Rowley¹⁵ models were used. The viscosity data were correlated by the Eyring-NRTL,¹⁶ Eyring-UNIQUAC¹⁷ and the two- and three-parameter McAlister¹⁸ models.

EXPERIMENTAL

Chemicals

MEA (99.5 %) was purchased from Merck, TEGDME (99.0 %) from Sigma–Aldrich, while PEG 200 (99.0 %) was supplied from Acros Organics. Chemicals were used without further purification. The densities, thermal conductivities and dynamic viscosities of the pure

substances have been compared in Table I with literature values at 298.15 K.¹⁹⁻²⁷ The agreement between literature and the experimental values is satisfactory with differences of less than 0.6 kg m⁻³ for the density measurements, within 5×10⁻³ W m⁻¹ K⁻¹ for the thermal conductivities, and within 7×10⁻² mPa s for the viscosity measurements of the less viscous fluids.

TABLE I. Densities ρ , thermal conductivities λ and dynamic viscosities η of the pure components at 298.15 K; standard uncertainties, u , for each variables are $u(T) = \pm 0.01$ K; $u(\rho) = \pm 5$ %; $u(x_1) = \pm 0.0001$, and the combined expanded uncertainties, U_c , are $U_c(\rho) = \pm 1.2$ kg m⁻³; $U_c(\lambda) = \pm 4.0$ % and $U_c(\eta) = \pm 1.0$ %, at the 0.95 level of confidence ($k \approx 2$)

Component	$\rho / 10^3 \text{ kg m}^{-3}$		$\lambda / \text{W m}^{-1} \text{K}^{-1}$		$\eta / \text{mPa s}$	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
MEA	1.0117	1.0123 ¹⁹	0.2349	0.2399 ^{a,20}	18.883	18.95 ²¹
TEGDME	1.0064	1.0059 ^{22,23} 1.0063 ²⁴	0.1649	0.1615 ²⁵	3.3316	3.313 ^{22,23} 3.394 ²⁴
PEG 200	1.1208	1.12098 ²⁶	0.2017 ^b	0.199 ^{b,27}	51.872	48.157 ²⁶

^aInterpolated value; ^bvalues at 303.15 K

Apparatus and procedures

Thermal conductivities reported in this study were measured using transient hot wire experimental setup, which is a reliable and precise technique for measuring the thermal conductivity of liquids.²⁸ The details are presented in the Supplementary material.

An analytical model for a long thin conductor heated by a constant current and cooled by the surrounding heat-conducting body of infinite dimensions can be found in the literature.^{29,30} The detailed considerations are given in Supplementary material to this paper.

Uncertainty in the measurement of the thermal conductivity was evaluated in accordance with the Guide to the expression of uncertainty in measurement (GUM).³¹ The obtained uncertainty components (for the calculations see Supplementary material) and the total expanded uncertainty of the performed thermal conductivity measurement are given in Table II.

TABLE II. Thermal conductivity measurement uncertainty components

Uncertainty component	Uncertainty level, %
u_a	2.5
u_σ	2.5
$u_{R_{w0}}$	0.2
u_{Z_R}	1.9
u_k	4.2

Viscosities η of the binary mixtures and corresponding pure substances were measured with a digital Stabinger SVM 3000/G2 viscometer. The instrument consists of two measuring cells; one of them is used for measuring the density of the sample and the other for the viscosity measurements. The principles of the measurements are presented in the Supplementary material. The temperature in the cell was regulated to ± 0.01 K with a built in solid-state thermostat. The reproducibility of the dynamic viscosity and density measurements, stated by the manufacturer, were 0.35 % and 0.5 kg m⁻³, respectively. The relative uncertainty in dynamic viscosity measurements was evaluated as less than ± 1.0 %, at the 0.95 level of confidence ($k \approx 2$). Densities of pure components were also measured with the Stab-

inger SVM 3000/G2 model. Uncertainty in density measurements, at the 0.95 level of confidence ($k \approx 2$), was estimated as $\pm 1.2 \text{ kg m}^{-3}$.

Mixtures were prepared gravimetrically on a Mettler AG 204 balance. The balance precision was $1 \times 10^{-7} \text{ kg}$ and the standard uncertainty in the mole fraction calculation was estimated as $\pm 1 \times 10^{-4}$.

RESULTS AND DISCUSSION

The experimental data of thermal conductivity λ and viscosity η , as well as the calculated values of deviation in thermal conductivity $\Delta\lambda$ and viscosity $\Delta\eta$ for investigated binary systems (MEA + TEGDME and MEA + PEG 200) at six temperatures, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K, and atmospheric pressure are reported in Table S-I of the Supplementary material.

The deviation functions were calculated from the equation:

$$\Delta Y = Y - \sum_{i=1}^2 x_i Y_i \quad (1)$$

in which ΔY refers to the deviation in the thermal conductivity, $\Delta\lambda$, or in the viscosity, $\Delta\eta$, Y is a mixture property, thermal conductivity or viscosity, while Y_i is thermal conductivity, λ_i , or viscosity, η_i , of the pure component.

The deviation functions $\Delta\lambda$ and $\Delta\eta$ were further correlated with the Redlich–Kister (RK) equation:¹¹

$$Z = x_i x_j \sum_{p=0}^k A_p \quad (2)$$

in which Z represents $\Delta\lambda$ or $\Delta\eta$, while A_p are the fitting parameters, optimized by the F -test, of which there are $(k+1)$. The values of fitting parameters are presented in Table S-II of the Supplementary material. The quality of the correlation was evaluated by the root-mean-square deviations (RMSD), σ . Literature values of the thermal conductivities for the pure components are also included in Fig. 2.

For monoethanolamine, the literature values show a similar temperature dependency as the obtained experimental data with a maximum deviation of around 2 %. The same is the case for TEGDME, except that the maximum deviation from the literature values for this substance was around 3.5 %.³² For PEG 200, no literature data are available, except for the values measured by one of the producers.²⁷ The experimental data decreased with increasing temperature, while literature values increased. In the investigated temperature range, the maximum deviation was 2.8 % at 323.15 K, while the minimum deviation was 0.5 % at 313.15 K.

Comparison of deviations in thermal conductivity, $\Delta\lambda$, is shown in Fig. 3 for both systems at 308.15 K. The deviations in thermal conductivity for investigated binary systems were negative at all temperatures and for all mixture compositions,

as presented in Table S-II and displayed in Fig. 3. Curves for both systems are asymmetrical and shifted towards higher MEA mole fractions. For both mixtures, the $\Delta\lambda$ values are more negative at higher temperatures, although the temperature influence was more significant in the MEA+TEGDME binary system. Mixture with PEG 200 showed higher deviation from ideality, as can be noticed in Fig. 3.

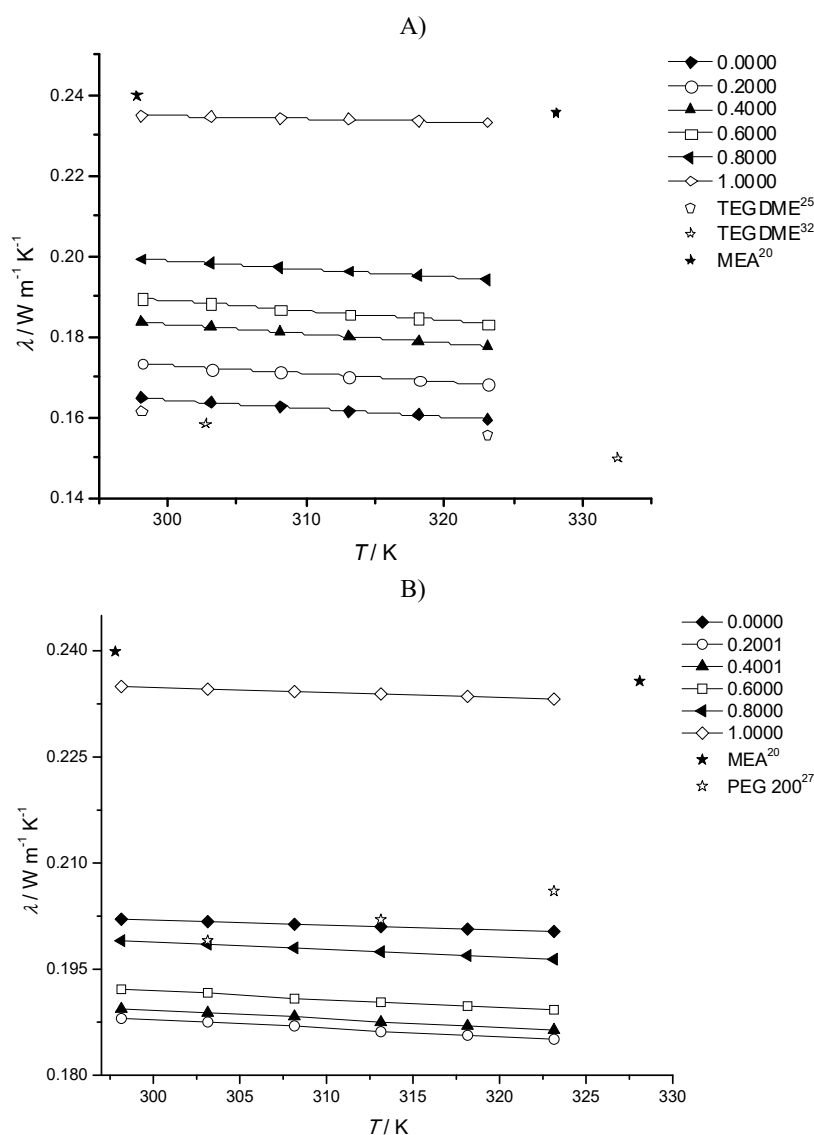


Fig. 2. Experimental values of the thermal conductivity λ , as a function of temperature for the systems: A) MEA+TEGDME and B) MEA+PEG 200, at different molar fractions, x_1 . Lines are fittings of the data points.

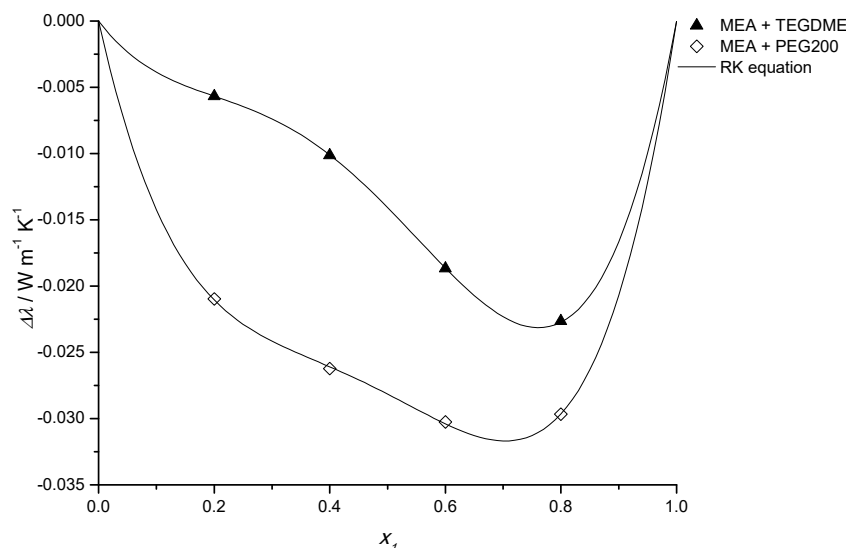


Fig. 3. Experimental values of the deviations in the thermal conductivity $\Delta\lambda$, as a function of MEA mole fraction x_1 for the MEA+TEGDME and MEA+PEG 200 systems at 308.15 K. The lines were calculated from the Redlich–Kister equation.¹¹

The experimental data for viscosity, η , and the calculated viscosity deviation, $\Delta\eta$, are presented in Figs. 4–6. Similar to the thermal conductivity, for system with TEGDME, the viscosities of mixtures were between the values for the pure components, while for the system with PEG 200, viscosities of the mixtures were higher than the viscosities of the pure components, as can be seen in Fig. 4B. The viscosities of both the mixtures and the pure components decreased with increasing temperature.

Literature values of the viscosity for pure MEA and PEG 200 were incorporated in Fig. 4. The agreement between the experimental data and literature values for MEA was very good, while for PEG 200, larger deviations were noticed. Inspection of the limited number of available data showed that one literature source reported lower²⁶ and the other higher²⁷ viscosity values than the ones measured in this study.

Viscosity deviations, $\Delta\eta$, were negative for the system with TEGDME and positive for the system with PEG 200, at all temperatures and for all mixture compositions, as can be seen in Fig. 6. The curves for both systems are asymmetrical and shifted towards the higher MEA mole fractions. For both mixtures, the $\Delta\eta$ values decreased by an absolute value with increasing temperature.

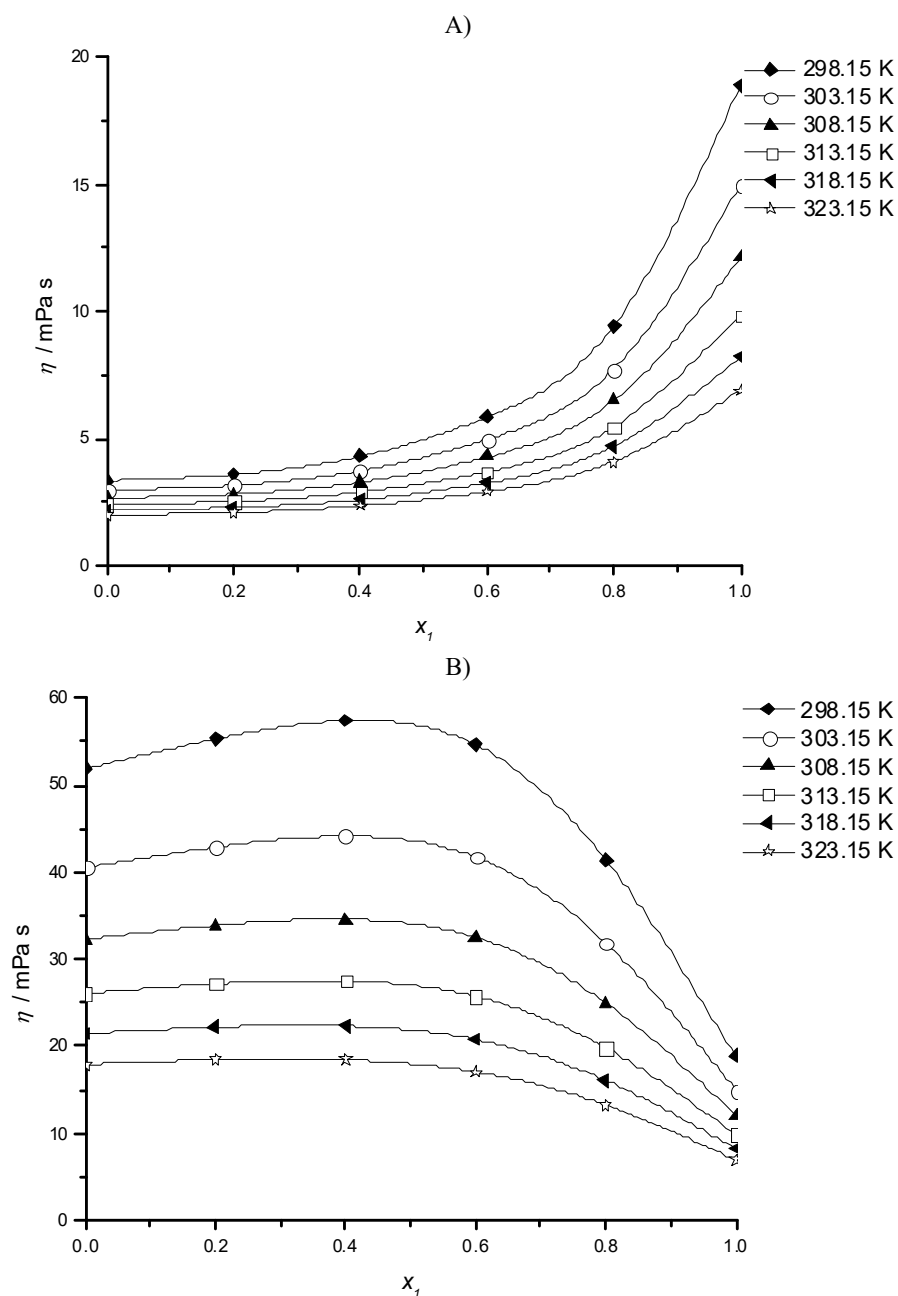


Fig. 4. Experimental values of viscosity η as a function of MEA mole fraction x_1 for the systems: A) MEA+TEGDME and B) MEA+PEG 200, at different temperatures. The lines were fitted to the data points.

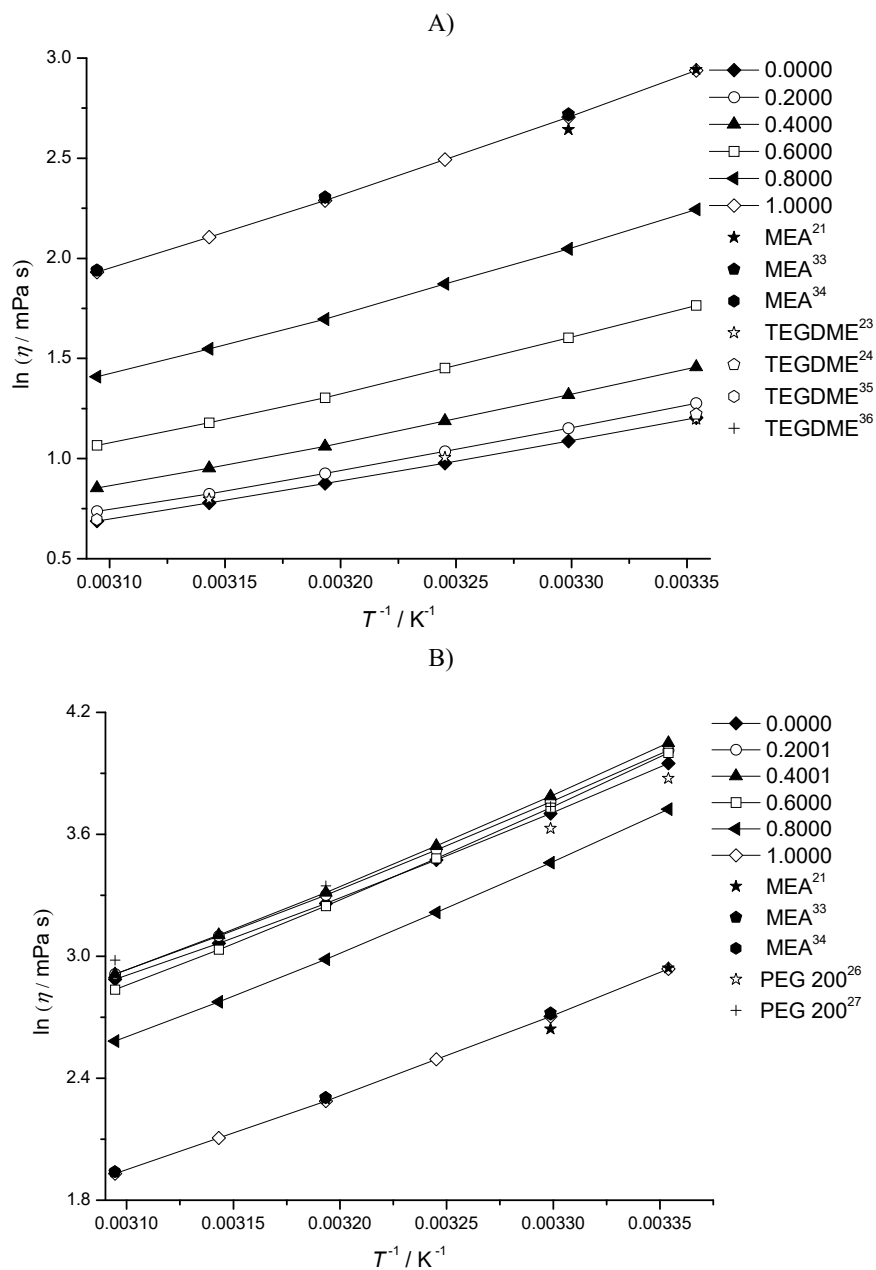


Fig. 5. Experimental values of viscosity η as a function of temperature for the systems: A) MEA+TEGDME and B) MEA+PEG200, at different MEA mole fractions x_1 . The lines were fitted to the data points.

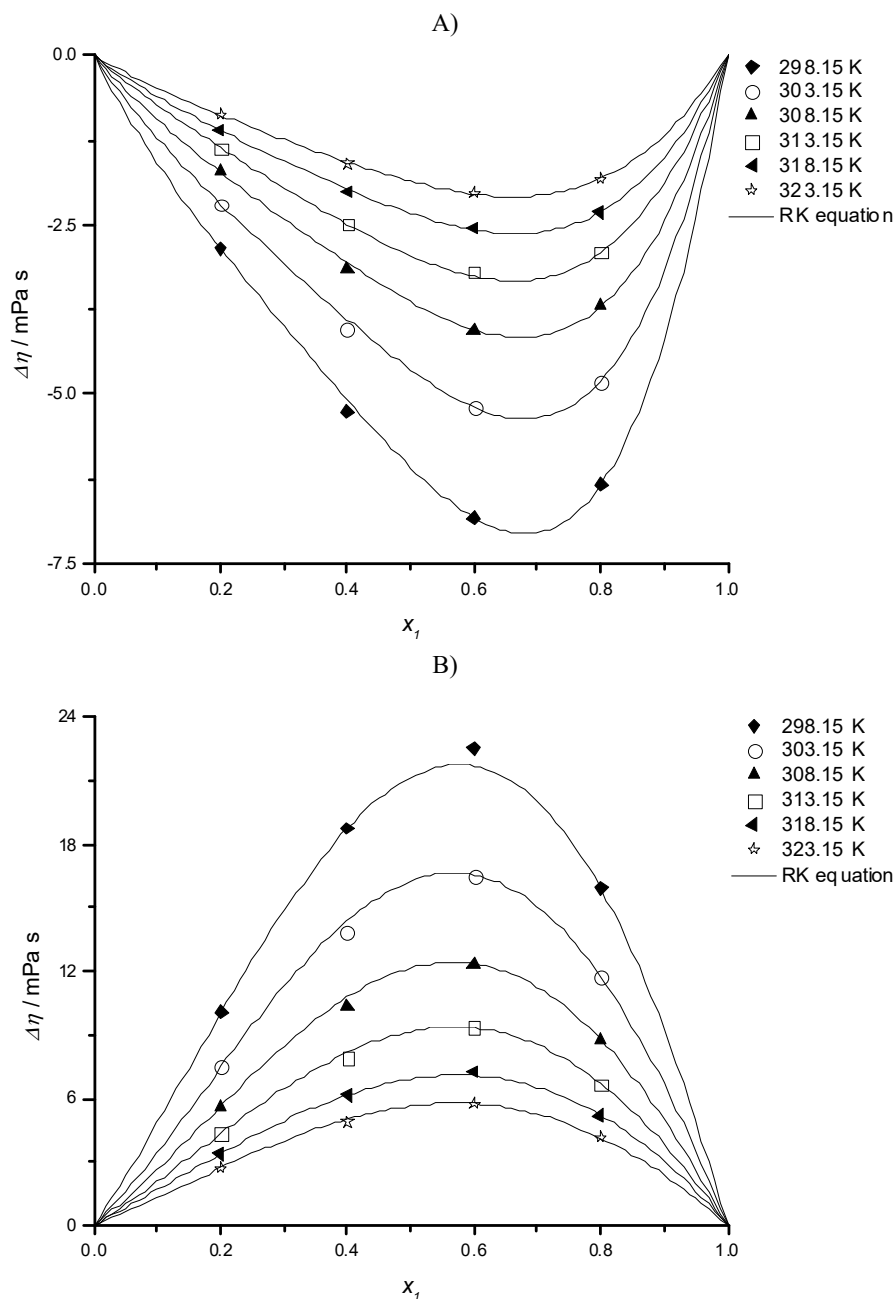


Fig. 6. Experimental values of the viscosity deviation $\Delta\eta$ as a function of the MEA mole fraction x_1 for the systems: A) MEA+TEGDME and B) MEA+PEG 200, at different temperatures. The lines were calculated from the Redlich-Kister equation.¹¹

Modelling

Thermal conductivities of mixtures were correlated using the Filippov,¹² Jamieson,¹³ Baroncini¹⁴ and Rowley¹⁵ models, while the viscosity data were correlated with the Eyring-NRTL¹⁶ Eyring-UNIQUAC¹⁷ and the McAllister 2-and 3-parameter¹⁸ models. Details of these models are given in the Supplementary material to this paper.

The ability of these models to correlate thermal conductivity and viscosity was estimated by calculating the percentage deviations (*PD*), from the following equation:

$$PD(Y) = \frac{100}{m} \sum_{i=1}^m \left| \frac{Y_{\text{exp}} - Y_{\text{cal}}}{Y_{\text{exp}}} \right|_i \quad (7)$$

in which Y_{exp} and Y_{cal} represent the experimental and calculated values, respectively, of the thermal conductivity or viscosity and m is the number of experimental data points.

The results of the modelling for the investigated binary mixtures are reported in Table III for the thermal conductivities and in Table IV for the viscosities.

TABLE III. Results of thermal conductivity correlations (*PD* / %)

<i>T</i> / K	Correlation			
	Filippov	Jamieson	Baroncini	Rowley
MEA (1)+TEGDME (2)				
298.15–323.15	2.05	1.97	5.19	2.43
MEA (1)+PEG 200 (2)				
298.15–323.15	2.56	1.88	5.47	7.11

TABLE IV. Results of the viscosity correlations (*PD* / %)

<i>T</i> / K	Correlation			
	Eyring-NRTL	Eyring-UNIQUAC	McAllister-3	McAllister-4
MEA (1)+TEGDME (2)				
298.15	0.29	1.40	0.27	0.16
303.15	0.14	1.35	0.11	0.10
308.15	0.21	1.34	0.21	0.14
313.15	0.21	1.00	0.22	0.12
318.15	0.18	1.05	0.14	0.09
323.15	0.24	0.92	0.23	0.07
MEA (1)+PEG 200 (2)				
298.15	4.59	0.79	2.15	0.21
303.15	3.70	0.68	2.09	0.23
308.15	2.78	0.60	1.97	0.21
313.15	2.03	0.55	1.88	0.22
318.15	1.36	0.45	1.80	0.22
323.15	1.07	0.38	1.79	0.24

The thermal conductivity correlations were realised with the same set of parameters over the complete temperature range investigated. Satisfactory results were obtained with the Filippov¹² and Jamieson¹³ models. The Baroncini¹⁴ model gave poorer results for both systems, while the Rowley model,¹⁵ both correlatively and predicatively, was satisfactory only for the system with TEGDME. Viscosity modelling was performed at each of the investigated temperatures. The best results in correlating viscosity were obtained with the three-parameter McAlister¹⁸ model, probably due to the larger number of adjustable parameters. The two-parameter Eyring-NRTL,¹⁶ Eyring-UNIQUAC¹⁷ and McAlister¹⁸ models mostly gave satisfactory results, with the exception of the Eyring-NRTL¹⁶ model for system with PEG 200 at lower temperatures.

CONCLUSIONS

Transport properties of two binary liquid mixtures were investigated both by measurement and by correlation to multiple models in order to gain better understanding of the conditions in liquid mixtures and to improve the models that describe their behaviour. The values of both properties decrease with an increase in temperature. The values of properties vary monotonically with composition for one system (MEA+TEGDME), but not for the other (MEA+PEG 200). In the latter case, the thermal conductivities were lower and the viscosities higher than the respective properties of the pure components. The thermal conductivity and viscosity data were successfully correlated with Filippov, Jamieson, Eyring-UNIQUAC and McAlister models. The Rowley and Eyring-NRTL models were satisfactory only for the MEA+TEGDME system, while the Baroncini model gave poorer results for both the investigated binary mixtures.

SUPPLEMENTARY MATERIAL

Considerations related to industrial gasses emission, experimental details and comments concerning correlation models are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД
 ТРАНСПОРТНА СВОЈСТВА БИНАРНИХ ТЕЧНИХ СМЕША – ПОТЕНЦИЈАЛНИХ
 РАСТВОРАЧА ЗА ОПТИМИЗОВАНИ ПРОЦЕС ПРЕЧИШЋАВАЊА ДИМНИХ ГАСОВА

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Топлотне проводљивости и вискозности три чисте супстанце, моноетаноламина (МЕА), тетраетиленгликол-диметил етра (ТЕGDМЕ) и полиетилен-гликола (РЕG 200) и две бинарне смеше (МЕА+ТЕGDМЕ и МЕА+РЕG 200) су измерене на 6 температура, 298,15; 303,15; 308,15; 313,15; 318,15 и 323,15 К, и на атмосферском притиску. Мерење топлотне проводљивости је засновано на нестационарној методи топле жице, док су вискозности одређене на дигиталном Stabinger SVM 3000/G2 вискозиметру. Из ових података, израчунате су промене топлотне проводљивости и вискозности при мешању и корелисане Redlich–Kister једначином. Топлотне проводљивости смеша корелисане су и моделима Filippov, Jamieson, Baroncini и Rowley док су за корелисање вискозности коришћени модели Eyring–UNIQUAC, Eyring–NRTL и McAlister па за испитивање великог броја променљивих са малим бројем експеримената.

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