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Densities, Viscosities, and Surface Tensions of Aqueous Mixtures of Sulfolane + Triethanolamine and Sulfolane + Diisopropanolamine

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ABSTRACT: Densities and viscosities of aqueous solutions containing sulfolane and ternary aqueous solutions of sulfolane and triethanolamine and ternary aqueous solutions containing sulfolane and disopropanolamine and also equilibrium surface tensions of the above ternary aqueous solutions were measured at temperatures ranging from (303.15 to 343.15) K and atmospheric pressure. The overall concentration of sulfolane, triethanolamine, and diisopropanolamine in solutions varied in the range of 0 to 16.5, 0 to 43, and 0 to 40 mass percent, respectively. Using the density, viscosity, and surface tension of pure water as the solvent, the corresponding experimental values obtained for the investigated solutions were correlated with temperature and concentration by a modified Setchenow equation.

INTRODUCTION

Alkanolamines, especially monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA), are the main constituents of aqueous solutions, which are currently in use in industrial natural gas treating and sweetening plants.[1] The process involves absorption followed by the chemical reaction of H_2S and CO_2 with the alkanolamine solution in a plate column at low temperatures (at about 315 K) and variable pressures (up to about 7 MPa). Aqueous solutions of a tertiary amine like TEA or MDEA are used for the selective removal of H_2S in the presence of CO_2, while the other alkanolamine solutions are used for the removal of CO_2.[2,3] Physical solvents such as sulfolane (SFL), 4-formylmorpholine (NFM), and triethylene glycol dimethyl ether (TEGDME) are nonreactive organic polar compounds that physically dissolve the acid gases. Because of their capability in the removal of acid gases CO_2 and H_2S from high-pressure gas streams they are of industrial importance and have been the subject of extensive studies during the last 25 years.[4,5] Solvent regeneration is done in the desorption stage of the process by reducing the pressure and requires less energy consumption than chemical solvents.[6] Physical solvents are less corrosive than chemical solvents because no chemical reaction takes place with the acid gases. Mixed solvents, which are formulations containing a chemical solvent and a physical solvent, combine the separate advantages of both solvents.[7] This way the limited stoichiometric capacity of the chemical solvent, which is restricted by chemical reaction between the alkanolamine and the acid gas (for example, in the case of MDEA the stoichiometric amount of H_2S or CO_2 absorbed into the solution is one mole per mole of MDEA) and works well at low pressures, is combined with the high capacity of a physical solvent (which is proportional to the partial pressure of the acid gas) and results in a solvent, which absorbs all acid gas compounds throughout the whole range of the acid gas partial pressures of interest.[7] The industrially important sulfinol process is one example in which a mixed solvent consisting of a diisopropanolamine (chemical component), sulfolane (physical component), and water is utilized.[8]

The physical properties such as density, viscosity, and surface tension of aqueous solutions of the alkanolamines as well as their mixture with physical solvents are necessary for the design of acid gas treatment equipment and for measuring and interpreting other physicochemical properties like the reaction kinetics of CO_2 and H_2S with aqueous amine solutions, liquid diffusivities, and free-gas solubilities.[9] Sacoo et al.[10] reported the experimental densities and viscosities of water—sulfolane mixtures over the whole mole fraction range at temperatures (303.15, 313.15, and 323.15) K. Yu et al.[11] reported the densities of water + sulfolane as well as water + tetraethylene glycol and benzene + tetraethylene glycol mixtures over the entire concentration range at 298.15 K and atmospheric pressure by using an oscillating tube densimeter. Finally Saleh et al.[12] reported the atmospheric pressure densities and viscosities of water + sulfolane mixtures in the entire composition range at temperatures ranging from (303.15 to 323.15) K. In case of TEA, Tseng and Thompson[13] reported densities and refractive indices of aqueous solutions in the entire composition range at (293.15, 298.15, and 303.15) K. Hawrylak et al.[14] also reported the densities, speed of sound, and other derived volumetric properties of aqueous solutions of alkanolamines including TEA at (298.15, 308.15, and 318.15) K and atmospheric pressure over the entire concentration range of the amine. They modeled the obtained excess volumes by the Redlich—Kister equation. Álvarez et al.[15] reported densities and viscosities of aqueous solutions of binary mixtures of some alkanolamines as well as 50 % in mass fraction aqueous solutions of TEA at temperatures ranging from (298.15 to 323.15) K.

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The surface tension of aqueous solutions of diethanolamine and triethanolamine over the entire concentration range at temperatures of (298.15 and 323.15) K was reported by Vázquez et al.[16] Álvarez et al.[17,18] also reported the surface tension of aqueous binary and ternary mixtures of some alkanolamines including DEA, TEA, and MDEA (at a concentration of up to 50 % in mass fraction) at temperatures from (298.15 to 323.15) K. In case of DIPA, Hikita et al.[19] reported the densities and viscosities of some aqueous alkanolamine solutions including DIPA at 298.15 K and atmospheric pressure, and Henni et al.[20] reported the results of the measurement of the density and viscosity of aqueous DIPA solutions over the entire mole fraction range from (298.15 to 343.15) K. To the best of our knowledge, there is no surface tension data reported in the open literature for pure or aqueous solutions of DIPA.

We are interested in studying the thermophysical properties of aqueous mixed solutions relevant to natural gas sweetening processes. In this work, the results of the measurement of nonthermal properties, that is, density, viscosity, and equilibrium surface tension of aqueous solutions of TEA + SFL and DIPA + SFL at temperatures from (303.15 to 343.15) K are reported. The obtained experimental data are correlated by a modified Setchenow equation.

EXPERIMENTAL SECTION

Materials. SFL (CAS Registry No. 126-33-0) and piperazine (CAS Registry No. 110-85-0) were obtained from Aldrich with a nominal mass purity > 99 %, and TEA (CAS Registry No. 102-71-6) and DIPA (CAS Registry No. 110-97-4) were supplied from Merck with a nominal mass purity > 99 % and > 98 %, respectively. All of the materials were used as purchased without further purification. Water used as solvent was distilled and deionized, which was degassed in an ultrasonic bath (FUNGILAB, model UA10MFD) at a temperature and wave frequency of 343 K and 50 kHz, respectively, for about 1 h prior to use. All solutions were prepared by the measurement of mass of the solutes and solvent on a calibrated balance (Mettler model AE 200) with an uncertainty ± 0.0001 g and measuring the volume of the solution by a standard volumetric flask up to 100 mL.

Apparatus and Procedure. The density was determined using a standard 25 mL glass pycnometer, which was calibrated with temperature by using water. An analytical balance (Mettler model AE 200) with an uncertainty ± 0.0001 g was used in density measurement. The pycnometer was placed inside of a dry glass vessel and the entire system was immersed in a thermostatic water bath (LAUDA, model ECOLINE E100) with temperature stability better than 0.02 K. The temperature of the pycnometer was measured with a Lutron model TM-917 digital thermometer with a 0.01 K resolution using a Pt-100 sensor inserted into the dry vessel. In general each density value reported was an average of three to five measurements, with the precisions of measurements being within ± 0.074 % (0.76 $\mathrm{kg \cdot m^{-3}}$).

The viscosity of aqueous solutions was determined using a standard Cannon-Fenske type capillary viscometer suitable for transparent liquids with kinematic viscosities in the range ($1.6 \cdot 10^{-6}$ to $8 \cdot 10^{-6}$) $\mathrm{m^2 \cdot s^{-1}}$ (size no. 75), and that of pure SFL and pure TEA was determined by Cannon-Fenske capillary viscometers size no. 100 and 350, respectively. The viscometer was suspended inside of a thermostatic water bath (Haake, model D8) with a temperature stability better than 0.05 K. The flow time was recorded manually using an electronic timer with an

Table 1. Review of the Literature Data for the Density, Viscosity, and Surface Tension of Water, Sulfolane, Triethanolamine, and the Water + Piperazine Mixture

	$\rho/\mathrm{kg \cdot m^{-3}}$		$\eta/\mathrm{mPa \cdot s}$		$\sigma/\mathrm{mN \cdot m^{-1}}$	
T/K	this work	lit (ref)	this work	lit (ref)	this work	lit (ref)
			Water			
303.15	996.00	995.647[a] 995.637[b] 995.65[c] 995.60[d]	0.797	0.7956[b] 0.7970[d]	71.24	71.20[h] 71.21[g]
313.15	991.70	992.215[a] 992.185[b] 992.21[c] 992.20[d]	0.653	0.6550[b] 0.6560[f] 0.6530[d]	69.92	69.52[g] 69.60[h]
323.15	987.40	988.037[a] 987.978[b] 988.04[c]	0.547	0.5460[b] 0.5470[c]	68.40	67.92[g] 67.94[h]
333.15	983.10	983.200[a] 983.12[c]	0.466	0.466[c] 0.476[f]	67.11	66.97
AAD %	0.043		0.358		0.367	
MAD %	0.069		2.10		0.712	
			Sulfolane			
303.15	1262.3	1262.02[k] 1262.331[l]	10.18	10.05201[k] 10.29[l]	47.95	
313.15	1254.0	1253.17[k] 1253.512[l]	7.85	7.78517[k] 7.947[l]	47.22	
323.15	1245.7	1244.21[k] 1244.701[l]	6.15	6.16449[k] 6.306[l]	46.61	
333.15	1236.5		4.40		45.74	
343.15	1229.0		3.57		45.16	
AAD %	0.055		1.18			
MAD %	0.121		2.47			
			Triethanolamine			
303.15	1119.6		405.6		45.13	45.16[i]
303.5				404.2[j]		
313.1		1112.3[j]				
313.15	1113.8		208.6		43.54	43.48[i]
313.5				203.4[j]		
323.15	1107.9		116.0		41.85	41.88[i]
333.15	1102.0		64.55		40.04	
333.5				65.50[j]		
333.9		1100.6[j]				
343.15	1096.2		38.79		38.11	
AAD %	0.113		1.43		0.099	
MAD %	0.135		3.46		0.149	
			Water + Piperazine (w = 0.0516)			
303.15	998.34	997.91[e]	0.959	0.97[e]	69.56	70.24[e]
313.15	993.90	994.40[e]	0.775	0.76[e]	67.98	68.51[e]
323.15	989.79	990.15[e]	0.641	0.62[e]	66.49	66.70[e]
333.15	985.10	985.24[e]	0.542	0.51[e]	65.17	65.26[e]
AAD %	0.042		3.17		0.550	
MAD %	0.066		6.23		0.972	

[a] Perry and Green.[21] [b] Álvarez et al.[15] [c] Henni et al.[22] [d] Comesaña et al.[23] [e] Muhammad et al.[24] [f] Bernal-Garcia et al.[25] [g] Álvarez et al.[18] [h] Lee et al.[28] [i] Vázquez et al.[16] [j] DiGuillo et al.[29] [k] Saleh et al.[12] [l] Sacco et al.[10]

Table 2. Density of Aqueous Sulfolane (SFL0 to SFL4) and Aqueous Ternary Mixtures of Sulfolane + Triethanolamine (TEA0 to TEA3) and Sulfolane + Diisopropanolamine (DIPA0 to DIPA2)[a]

		$\rho/\mathrm{kg \cdot m^{-3}}$				
solution	$w_{\mathrm{SFL}}/w_{\mathrm{amine}}$	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
				Sulfolane		
SFL0	0.0346/0	1003 ± 0.3	999.7 ± 2.3	995.2 ± 1.7	990.1 ± 1.9	984.3 ± 1.2
SFL1	0.0487/0	1007 ± 0.2	1003 ± 0.1	998.2 ± 0.5	993.0 ± 0.5	987.0 ± 3.5
SFL2	0.0721/0	1012 ± 0.1	1007 ± 0.3	1003 ± 0.4	998.9 ± 0.3	991.7 ± 1.0
SFL3	0.1022/0	1020 ± 0.3	1016 ± 0.5	1010 ± 0.3	1005 ± 1.8	998.0 ± 1.1
SFL4	0.1635/0	1038 ± 6.0	1032 ± 0.6	1026 ± 0.2	1020 ± 0.8	1012 ± 1.2
				Sulfolane/Triethanolamine		
TEA0	0/0.4227	1052 ± 0.1	1048 ± 0.2	1043 ± 0.6	1037 ± 1.3	1032 ± 0.6
TEA1	0.0406/0.4188	1058 ± 0.5	1054 ± 0.3	1049 ± 0.7	1045 ± 0.3	1040 ± 0.8
TEA2	0.0962/0.3464	1059 ± 1.4	1057 ± 0.1	1051 ± 1.0	1046 ± 0.3	1041 ± 0.6
TEA3	0.1347/0.2794	1064 ± 0.8	1058 ± 0.2	1054 ± 0.2	1049 ± 0.8	1042 ± 0.5
				Sulfolane/Diisopropanolamine		
DIPA0	0/0.3873	1016 ± 0.7	1012 ± 0.4	1006 ± 0.2	1000 ± 0.9	994.5 ± 0.2
DIPA1	0.0993/0.3205	1030 ± 1.1	1026 ± 0.5	1021 ± 0.3	1014 ± 0.6	1009 ± 0.3
DIPA2	0.1417/0.2630	1034 ± 0.7	1030 ± 0.4	1025 ± 0.2	1019 ± 0.2	1013 ± 0.3

[a] Values after ± are the associated standard deviation resulting from at least three density measurements.

uncertainty ± 0.01 s. Each viscosity value reported was an average of four to eight measurements, and the precisions of measurements are within ± 0.66 % (0.011 mPa·s).

The surface tension measurements were carried out using a LAUDA tensiometer model (TD3), which operated on the basis of the du Noüy ring method. The ring employed was a commercial platinum−iridium ring supplied by LAUDA, and it was cleaned with water and acetone and flame-dried before each measurement. The samples were stirred in a closed measurement vessel to prevent evaporation. The temperature of the measurement vessel was controlled by connection to a thermostat-cryostat bath (LAUDA PTT) with a temperature stability of 0.1 K. In general each surface tension value reported was an average of 10 measurements with the uncertainty of measurements being within ± 0.34 % (0.17 mN·m^{-1}).

It must be pointed out that the surface tension of mixtures is always sensitive to the different volatility of components especially at high temperatures. To lessen this effect, immediately before each measurement, the masses were readjusted to the initially prepared samples by adding an adequate amount of water in a minimum time. The amount of water added in each measurement (less than 1 g) was so low relative to the mass of the mixtures (about 50 g) that it did not disturb the thermal equilibrium of the system at all. Because of high boiling points of piperazine (418.15 K), SFL (558.15 K), TEA (633.15 K), and DIPA (522.15 K), it is a reasonable assumption that water is the only component of aqueous solutions, which is lost and evaporated in the temperature range studied in this work.

All measurements were carried out in the temperature range of (303.15 to 343.15) K with 10 K steps.

■ RESULTS AND DISCUSSION

Density. To validate the quality of compounds and ensure that the experimental procedure employed for the measurement of density gives suitable values, the densities of pure water, SFL, and TEA, as well as w = 0.0516 piperazine aqueous solution were measured at (303.15, 313.15, 323.15, and 333.15) K and compared with literature values. The obtained experimental data as well as the reported literature values are summarized in Table 1. The comparison shows that the obtained experimental density data are in good agreement (within 0.14 %) with the corresponding values reported in other reliable sources.[15,21−23] The experimental average densities of aqueous SFL solutions (SFL0 to SFL4), TEA (TEA0), and DIPA (DIPA0) as well as the ternary aqueous mixture of SFL with TEA (TEA1 to TEA3) and SFL with DIPA (DIPA1 and DIPA2) obtained in this work at temperatures of (303.15, 313.15, 323.15, 333.15, and 343.15) K, together with their corresponding standard deviations (values after ± in the table), resulting from at least three measurements of the density are summarized in Table 2. It can be observed that the density of all mixtures decreases by increasing temperature, and the density of all mixtures studied is greater than that of water at the same temperature. In the case of the aqueous solution of SFL the density increases by increasing the mole fraction of SFL in solution. In general, at each temperature, the density of aqueous SFL + TEA solutions are greater than that of the corresponding aqueous SFL + DIPA solutions with the same mass fraction.

The obtained experimental density values were correlated using a Setchenow type equation.[26] Originally the empirical Setchenow equation was employed to express the salting-in and salting-out of volatile solutes into aqueous solutions of a salt.[26]

$$\ln S_{ia} = \ln \frac{x_{ia}}{x_{iw}} = k_i C_i \qquad (1)$$

where S_{ia} is the salting in/out ratio, x_{ia} and x_{iw} are, respectively, the solubilities expressed in mole fraction of the volatile solute or gas in the aqueous salt solution and in salt-free pure solvent (water), k_i is the salting parameter, and C_i is the concentration of the salt (expressed in molar, molality, mole fraction, etc.) in the

Table 3. Numerical Values of the Density, Viscosity, and Surface Tension of Water as a Function of Temperature

T	ρ[a]	η[b]	σ[c]
K	kg·m^{-3}	mPa·s	mN·m^{-1}
303.15	0.99570	0.7980	71.26
313.15	0.99231	0.6537	69.56
323.15	0.98809	0.5481	67.86
333.15	0.98321	0.4674	66.16
343.15	0.97783	0.4057	64.46

[a] Henni et al.[22] [b] NIST.[30] [c] Vargaftik et al.[31]

Table 4. Density, Viscosity, and Surface Tension Parameters a_i and b_i (in eqs 2 and 3) for the Aqueous Solution of Sulfolane and Aqueous Ternary Mixtures of Sulfolane + Triethanolamine and Sulfolane + Diisopropanolamine

	density		viscosity		surface tension	
i	a_i	b_i	a_i	b_i	a_i	b_i
1	2.671699	−0.007502	−5.598040	0.021736	−1.173738	0.001847
2	0.118836	0.000225	0.619490	0.002313	−1.817322	0.004795
3	0.159049	−0.000577	−6.137589	0.036672	−3.735302	0.008786
4	0.047012	0.000288	15.031178	−0.043780	0.224150	−0.001328
5	0.856996	−0.002119	8.814676	0.001137	1.672892	0.005370
6	−0.215214	0.000603	15.059454	−0.045054	−1.530445	−0.002981
7	−0.084895	0	3.931441	0	−1.387018	0
8	−0.041241	0	3.839141	0	1.764991	0

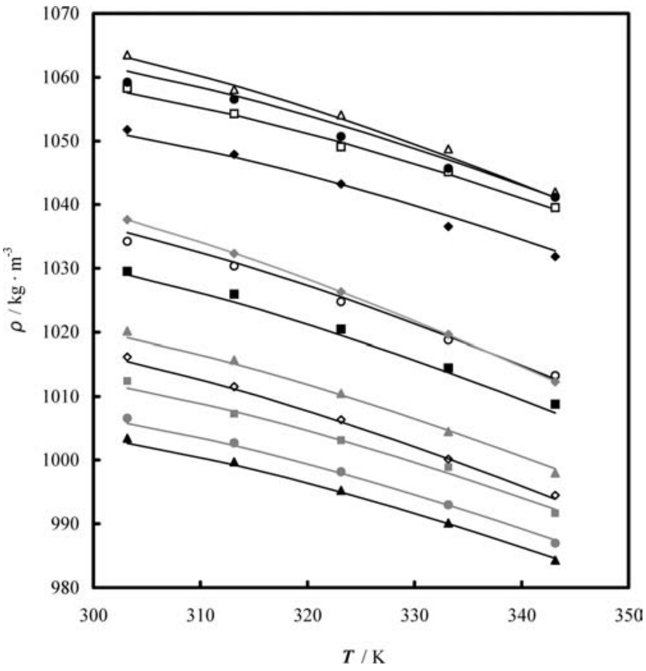

Figure 1. Experimental and correlated densities, ρ, as a function of temperature for ▲, SFL0; gray ●, SFL1; gray ■, SFL2; gray ▲, SFL3; gray ◆, SFL4; ◆, TEA0; □, TEA1; ●, TEA2; △, TEA3; ◇, DIPA0; ■, DIPA1; ○, DIPA2; and —, calculated from eq 2.

aqueous solution. The Setchenow equation has previously been employed by some researchers to model the solubility of light hydrocarbons in aqueous alkanolamine solutions.[27] In this work the Setchenow equation (eq 1) has been adapted to correlate the obtained experimental density, viscosity, and surface tension data. Here we have assumed that the presence of one or more solutes in water gives rise to an increase or decrease in the property of interest. Thus, the solubility ratio x_{ia}/x_{iw}, in eq 1 is replaced by the density, viscosity, or surface tension ratio, and the right-hand side of this equation is extended to include both linear and quadratic terms for the concentration of every solute present in the solution:

$$\ln \frac{P_s}{P_w} = k_1 C_1^2 + k_2 C_1 + k_3 C_2^2 + k_4 C_2 + k_5 C_3^2 + k_6 C_3 + k_7 C_1 C_2 + k_8 C_1 C_3 \qquad (2)$$

where P_s and P_w are, respectively, the relevant physical property of the solution containing components i with concentration C_i, and physical property of pure solvent (here water). It must be mentioned that in eq 2, C_i stands for the concentration of component i expressed as molar concentration, mass fraction, molar fraction, and so forth, but here C_1, C_2, and C_3 stand for the mass fractions of SFL, TEA, and DIPA, respectively. Thus, for aqueous TEA (TEA0 in Tables 2, 5, and 6) or aqueous DIPA (DIPA0 in Tables 2, 5, and 6) solutions $C_1 = 0$, for aqueous SFL + TEA (TEA1 to TEA3 in Tables 2, 5, and 6) solutions $C_3 = 0$ and for aqueous SFL + DIPA (DIPA1 and DIPA2 in Tables 2, 5, and 6) solutions $C_2 = 0$. The numerical values for the density of pure water at each temperature were extracted from ref 22 and are summarized in Table 3 for convenience of the reader. k_i in eq 2 are pair parameters and are assumed to be linearly dependent on temperature except for the cross-terms, which were assumed to be independent of temperature:

$$k_i = a_i + b_i(T/\mathrm{K}) \qquad (3)$$

The units of the a_i and b_i parameters depend on the concentration scale, C_i, which is used in eq 2. The a_i and b_i parameters were evaluated by applying the nonlinear least-squares fitting procedure to obtain experimental density data in the temperature range (303.15 to 343.15) K, and their values are tabulated in Table 4. Choosing the mass fraction of each component for expressing the concentration C_i in eq 2 yielded the best agreement between correlated and experimental values. The average of relative deviations, ARD %, defined by eq 4 and maximum of relative deviations, MRD %, defined by eq 5 for a number of N experimental points are, respectively, 0.04 % and 0.11 % for aqueous SFL, 0.07 % and 0.16 % for aqueous SFL + TEA, and 0.07 % and 0.13 % for aqueous SFL + DIPA solutions.

$$\mathrm{ARD}\% = \frac{100}{N} \sum_{i=1}^{N} \frac{|P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}}|}{P_i^{\mathrm{exp}}} \qquad (4)$$

$$\mathrm{MRD}\% = \mathrm{maximum}\left(\frac{|P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}}|}{P_i^{\mathrm{exp}}} \cdot 100\right) \qquad (5)$$

P_i^{cal} and P_i^{exp} in eqs 4 and 5 stand for the calculated using eq 2 and experimental value of the physical property of interest, respectively. The correlated densities of solutions (continuous solid lines) as a function of temperature are compared with the obtained experimental density values (symbols) in Figure 1. The values of ARD %, MRD %, and Figure 1 altogether show that

Table 5. Viscosity of Aqueous Sulfolane (SFL0 to SFL4) and Aqueous Ternary Mixtures of Sulfolane + Triethanolamine (TEA0 to TEA3) and Sulfolane + Diisopropanolamine (DIPA0 to DIPA2)[a]

		η/mPa·s				
solution	$w_{\mathrm{SFL}}/w_{\mathrm{amine}}$	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
				Sulfolane		
SFL0	0.0346/0	0.84 ± 0.006	0.69 ± 0.001	0.58 ± 0.003	0.49 ± 0.002	0.43 ± 0.003
SFL1	0.0487/0	0.85 ± 0.008	0.70 ± 0.008	0.59 ± 0.009	0.50 ± 0.013	0.44 ± 0.002
SFL2	0.0721/0	0.88 ± 0.003	0.73 ± 0.001	0.61 ± 0.002	0.52 ± 0.003	0.45 ± 0.002
SFL3	0.1022/0	0.92 ± 0.005	0.76 ± 0.004	0.64 ± 0.002	0.55 ± 0.004	0.48 ± 0.002
SFL4	0.1635/0	1.02 ± 0.004	0.84 ± 0.003	0.71 ± 0.003	0.61 ± 0.002	0.54 ± 0.001
				Sulfolane/Triethanolamine		
TEA0	0/0.4227	4.13 ± 0.009	2.91 ± 0.020	2.16 ± 0.006	1.67 ± 0.005	1.36 ± 0.003
TEA1	0.0406/0.4188	4.51 ± 0.017	3.25 ± 0.019	2.41 ± 0.015	1.86 ± 0.008	1.43 ± 0.003
TEA2	0.0962/0.3464	3.49 ± 0.016	2.59 ± 0.017	1.95 ± 0.006	1.50 ± 0.009	1.21 ± 0.015
TEA3	0.1347/0.2794	2.71 ± 0.009	1.93 ± 0.026	1.51 ± 0.003	1.21 ± 0.007	0.98 ± 0.001
				Sulfolane/Diisopropanolamine		
DIPA0	0/0.3873	5.42 ± 0.030	3.74 ± 0.029	2.56 ± 0.028	1.88 ± 0.035	1.42 ± 0.001
DIPA1	0.0993/0.3205	4.21 ± 0.026	2.92 ± 0.098	2.14 ± 0.019	1.61 ± 0.016	1.22 ± 0.003
DIPA2	0.1417/0.2630	3.15 ± 0.046	2.26 ± 0.023	1.67 ± 0.006	1.30 ± 0.007	1.04 ± 0.006

[a] Values after ± are the associated standard deviation resulting from at least four viscosity measurements.

there exists quite good agreement between obtained experimental data and correlated density values.

An analysis of ARD % values concerning the neglect of each of k_i in eq 2 for the correlation of experimental densities reveals that: (1) The coefficients of quadratic terms k_1 and k_3 are of minor importance compared to the coefficients of linear terms k_2 and k_4 for SFL and SFL + TEA solutions, that is, by setting $k_1 = 0$ or $k_3 = 0$, values of ARD % increase by an order of magnitude for SFL and SFL + TEA solutions, whereas setting $k_2 = 0$ or $k_4 = 0$ results in 2 orders of magnitude increase in ARD %. (2) The reverse is true for SFL + DIPA aqueous solutions, namely, the coefficient of the quadratic term k_5 is more important than that of the linear term k_6. (3) The coefficients of the cross terms k_7 and k_8 are less important compared to other coefficients for all of the ternary mixtures, that is, by setting $k_7 = 0$ or $k_8 = 0$, values of ARD % increase to 0.22 % and 0.09 % for aqueous SFL + TEA and SFL + DIPA solutions, respectively.

Viscosity. The viscometer constant, that is, the ratio $\eta/\rho t$, which showed quiet good linear correlation ($R^2 > 0.99$) with temperature, was evaluated through calibration with pure water at temperatures from (303.15 to 343.15) K. Comparing the viscosities obtained for pure water, SFL, and TEA, as well as $w = 0.0516$ aqueous piperazine solution with the corresponding values reported by other researchers[15,22−25] validated the quality of compounds and the method of measurement. Table 1 shows that the viscosity values obtained in this work for pure water, SFL, TEA, and aqueous piperazine solution are, respectively, within 2.1 %, 2.5 %, 3.5 %, and 3.2 % of the experimental data reported in the literature. The average viscosity values obtained in this work together with the standard deviations resulting from at least four measurements for aqueous SFL as well as aqueous SFL + TEA and aqueous SFL + DIPA solutions at temperatures (303.15, 313.15, 323.15, 333.15, and 343.15) K are presented in Table 5. It can be seen that the viscosity of all aqueous solutions decreases as the temperature increases. The viscosity of aqueous sulfolane solution increases by increasing the concentration of SFL at each specified temperature. In general the viscosity of aqueous solutions containing diisopropanolamine is greater than that of the aqueous triethanolamine solutions with the same molar concentration of components at each specified temperature. The viscosity data obtained in this work was correlated using the extended Setchenow equation (eq 2). The parameters a_i and b_i of the Setchenow equation were estimated by applying the

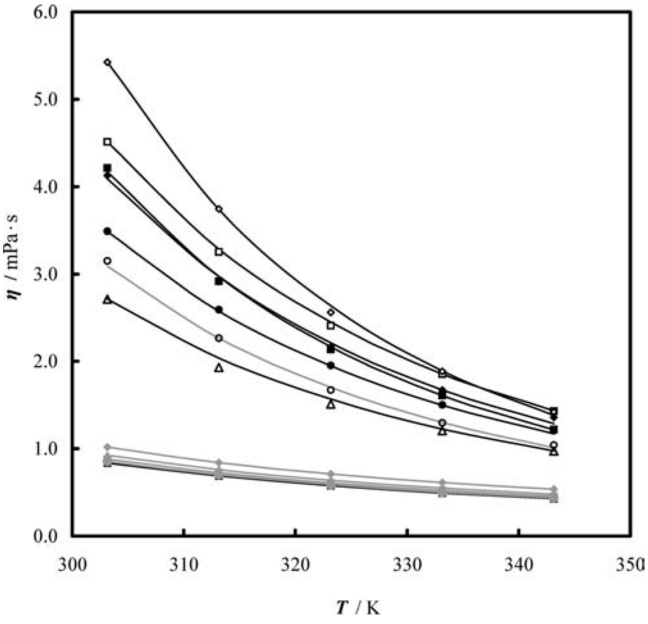

Figure 2. Experimental and correlated viscosities, η, as a function of temperature for ▲, SFL0; gray ●, SFL1; gray ■, SFL2; gray ▲, SFL3; gray ◆, SFL4; ◆, TEA0; □, TEA1; ●, TEA2; △, TEA3; ◇, DIPA0; ■, DIPA1; ○, DIPA2; and —, calculated from eq 2.

Table 6. Surface Tension of Aqueous Ternary Mixtures of Sulfolane + Triethanolamine (TEA0 to TEA3) and Sulfolane + Diisopropanolamine (DIPA0 to DIPA2)[a]

		σ/mN·m^{-1}				
solution	w_{SFL}/w_{amine}	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
				Sulfolane/Triethanolamine		
TEA0	0/0.4227	54.5 ± 0.3	53.8 ± 0.1	53.0 ± 0.1	52.3 ± 0.3	51.4 ± 0.1
TEA1	0.0406/0.4188	52.6 ± 0.1	52.0 ± 0.2	51.4 ± 0.1	50.7 ± 0.2	49.9 ± 0.4
TEA2	0.0962/0.3464	53.9 ± 0.1	53.2 ± 0.2	52.5 ± 0.1	51.8 ± 0.1	50.9 ± 0.1
TEA3	0.1347/0.2794	55.6 ± 0.1	54.9 ± 0.03	54.1 ± 0.3	53.3 ± 0.1	52.3 ± 0.1
				Sulfolane/Diisopropanolamine		
DIPA0	0/0.3873	45.3 ± 0.2	44.4 ± 0.2	43.2 ± 0.3	42.1 ± 0.1	40.5 ± 0.1
DIPA1	0.0993/0.3205	46.5 ± 0.4	45.4 ± 0.3	44.6 ± 0.3	43.0 ± 0.1	42.1 ± 0.4
DIPA2	0.1417/0.2630	47.0 ± 0.2	46.4 ± 0.04	45.6 ± 0.3	44.5 ± 0.1	43.1 ± 0.1

[a] Values after ± are the associated standard deviation resulting from 10 surface tension measurements.

nonlinear least-squares fitting procedure to obtained experimental viscosity data in the temperature range (303.15 to 343.15) K and their values are presented in Table 4. The best agreement between correlated and experimental values was achieved by choosing the mass fraction of components in the solution as the concentration scale in eq 2 with ARD % and MRD % being, respectively, 0.10 % and 0.41 % for aqueous sulfolane, 1.4 % and 5.6 % for aqueous SFL + TEA, and 1.2 % and 2.9 % for aqueous SFL + DIPA solutions. Also in Figure 2 the experimental and correlated viscosity values as a function of temperature are compared with each other. It must be emphasized that the viscosity values presented by the National Institute of Standards and Technology (NIST)[30] for pure water was employed for the evaluation of parameters a_i and b_i of the Setchenow equation.

The following conclusions can be inferred from the analysis of ARD % values for viscosity of ternary aqueous solutions: (1) The coefficient of quadratic term k_1 is of minor importance compared to the coefficient of linear term k_2 for aqueous SFL solutions, that is, by setting $k_1 = 0$, the value of ARD % increase from 0.10 to 1.26, while in case $k_2 = 0$, it increases to 10.7. (2) The reverse is true for SFL + TEA and SFL + DIPA aqueous solutions; namely, the coefficients of the quadratic terms, k_3 and k_5, are much more important than that of the linear terms k_4 and k_6. Thus, $k_3 = 0$ or $k_5 = 0$ results in ARD % = 52.8 and 61.0, but in case $k_4 = 0$ or $k_6 = 0$ results in ARD % = 25.5 and 17.8 for ternary mixtures of water + SFL + TEA and water + SFL + DIPA, respectively. (3) Neglecting the coefficients of the cross terms, that is, setting $k_7 = k_8 = 0$, values of ARD % increase to 8.23 and 8.74 for aqueous SFL + TEA and SFL + DIPA solutions, respectively.

Surface Tension. To validate the experimental procedure employed for measurement of the surface tension of solutions studied in this work, the surface tension of pure water, SFL, TEA and $w = 0.0516$ solution of piperazine in water at temperatures (303.15, 323.15, 333.15, and 343.15) K was measured and compared with the corresponding values reported in the literature (Table 1).[18,24,28] It can be observed from Table 1 that the experimental surface tension values measured in this work agree quite well with the reported literature data (within 1 %) for the above-mentioned systems. The experimental average surface tensions of ternary aqueous mixture of SFL with TEA and SFL with DIPA obtained in this work at temperatures (303.15, 313.15, 323.15, 333.15, and 343.15) K, together with their corresponding standard deviations, resulting from 10 measurements of the surface tension of the studied systems are summarized in Table 6 and Figure 3. It can be seen that the surface tension of all mixtures decreases by increasing temperature, and the surface tension of all mixtures studied are less than that of water at the same temperature. In general, at a given temperature, the surface tension of aqueous SFL + TEA solutions is greater than that of the corresponding aqueous SFL + DIPA solutions with the same molar concentration.

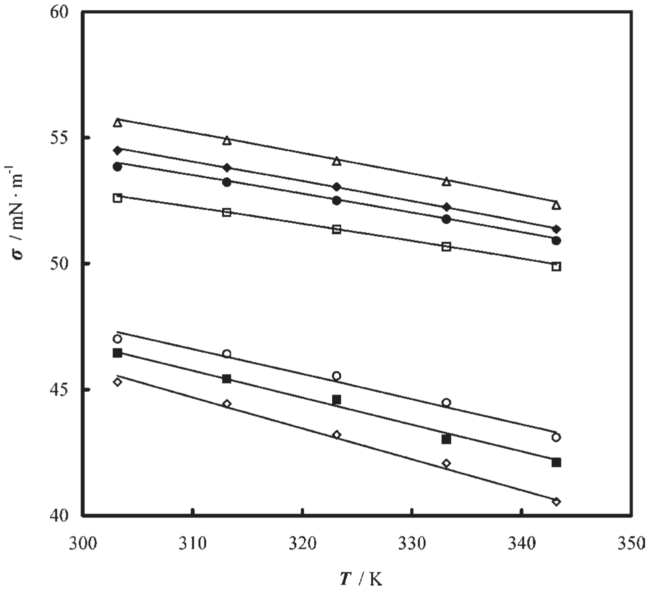

Figure 3. Experimental and correlated surface tensions, σ, as a function of temperature for ◆, TEA0; □, TEA1; ●, TEA2; △, TEA3; ◇, DIPA0; ■, DIPA1; ○, DIPA2; and —, calculated from eq 2.

As in the case of density and viscosity, the obtained experimental surface tension values were correlated using the extended Setchenow equation. This way the surface tension values presented in ref 31 for pure water were employed for evaluating the parameters a_i and b_i of the Setchenow equation. The best agreement between the obtained experimental surface tension data and correlated values was achieved by choosing the mass fraction concentration scale in eq 2. The values of the parameters a_i and b_i for correlating experimental surface tension values are tabulated in Table 4. The ARD % and MRD % values are 0.11 %

and 0.29 % for aqueous SFL + TEA and 0.37 % and 0.58 % for aqueous SFL + DIPA systems, respectively.

Again considering the ARD % as a criterion for deducing the importance of coefficients k_i, the following conclusions can be made about correlative capability of eq 2 for the experimental surface tension of ternary aqueous solutions: (1) Putting $k_1 = 0$ or $k_2 = 0$ results in a minor increase in ARD % for SFL + TEA and SFL + DIPA solutions. However, the coefficient of the linear term k_2 is of higher importance than that of the quadratic term k_1. (2) The coefficient of quadratic term for TEA, k_3, is more important than that of linear term k_4; thus, putting $k_3 = 0$ results in a great increase in ARD % from 0.11 to 13.4, while putting $k_4 = 0$ results in an increase of ARD % from 0.37 to 7.92. (3) The reverse is true for SFL + DIPA aqueous solutions; namely, the coefficient of the quadratic term, k_6 is much more important than that of the linear term k_5. Thus, setting $k_5 = 0$ results in ARD % = 30.2, but setting $k_6 = 0$ results in ARD % = 125.9. (4) Neglecting the coefficients of the cross terms, that is, setting $k_7 = 0$ or $k_8 = 0$, values of ARD % increase to 3.23 and 4.06 for aqueous SFL + TEA and SFL + DIPA solutions, respectively.

A point needs to be clarified here about the model expressed by eq 2. Although eq 2 is general and it can potentially be used to correlate the experimental physical properties of quaternary solutions (mixtures of water + SFL + TEA + DIPA) as well, because the cross term $k_9C_2C_3$, which accounts for the interaction of TEA and DIPA in the mixture, is not determined here, it must not be expected to produce the physical properties with the same accuracy as that of the ternary mixtures. One may apply this only to calculate a rough estimate of the physical property for quaternary mixtures. However the model expressed by eq 2 can be used to correlate the experimental physical properties of binary aqueous solutions of TEA and DIPA with good accuracy. The ARD % and MRD % for the density of TEA0 are 0.08 and 0.16 and for DIPA0 are 0.04 and 0.07, respectively. The corresponding values for viscosity of TEA0 are 2.1 and 5.1 and for DIPA0 are 1.3 and 2.9, respectively. In case of surface tension, the values of ARD % and MRD % for TEA0 are 0.06 and 0.17 and for DIPA0 are 0.39 and 0.56, respectively.

■ CONCLUSIONS

The nonthermal physical properties, that is, the density, viscosity, and surface tension of water + triethanolamine + sulfolane and water + diisopropanolamine + sulfolane mixtures, which are in use in the natural gas sweetening processes, were measured in this work. The Setchenow equation was modified and extended for the first time to correlate the experimental thermophysical properties of multicomponent solutions. The presented approach, which is easy to use, is applicable directly to the experimental data of multicomponent mixtures and requires only the corresponding thermophysical properties of pure solvent at the given temperature without a need for the thermophysical properties of binary pairs of constituents that make the solution. The presented approach is applicable to correlate other thermophysical properties like the heat capacity and thermal conductivity of multicomponent solutions.

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