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Vapor-Pressure Measurements of Liquid Solutions at Different Temperatures: Apparatus for Use over an Extended Temperature Range and Some New Data

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An apparatus for the measurement of vapor pressures of pure solvents and solutions at different temperatures is described. The apparatus is tested for the temperature range (298.15 to 363.15) K using pure water and aqueous NaCl solutions. The vapor pressures are presented for methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, ranging from temperatures 298.15 K up to the boiling points of these alcohols. The vapor-pressure data of pure alcohols are correlated with the Antoine equation. The results are compared with literature values.

1. Introduction

Precise vapor-pressure measurements yield valuable thermodynamic data, such as osmotic or activity coefficients of solutions. At room temperature, numerous systems have been measured[1,2] over a wide concentration range, at least as far as aqueous solutions are concerned. For higher temperatures, however, the amount of available data is still insufficient. For example, it would be useful to have more data for the prediction of thermodynamic properties of electrolytes in mixed solvents,[3−5] in high-energy batteries,[6] for the optimization of separation processes, water pollution control, salting-in and salting-out effects, for the production of natural gas, for food production, and the production of fertilizers.[7]

From the literature, several set ups are known.[8−16] Most of them have restricted temperature or pressure ranges, have difficulties in the experimental handling, or cannot neglect the effect of the vapor pressure of mercury on the measured vapor pressure. Therefore, we decided to build an apparatus that allows the determination of vapor pressures over a wide temperature range, at least from room temperature up to 473 K.

Barthel and Neueder constructed a static-type apparatus,[17] and the vapor pressures of some salts in methanol, ethanol, acetonitrile, acetone, and 2-propanol[18−26] were measured with an uncertainty of ±0.3 Pa in pressure and $\pm 3 \times 10^{-4}$ K in temperature at 298.15 K. This apparatus only permits measurements in a temperature range from (293 to 303) K. A new version of this apparatus was constructed, which allows the measurement of vapor pressures of pure fluids and of electrolyte solutions over a wide temperature range, namely, from (278 to 473) K.

The apparatus was tested from (298.15 to 363.15) K using pure water[27,28] and aqueous NaCl solution.[8] The measured data were compared with literature values.[8] The vapor pressure of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol from 298.15 K up to the boiling points of these alcohols were measured and correlated with the Antoine equation.

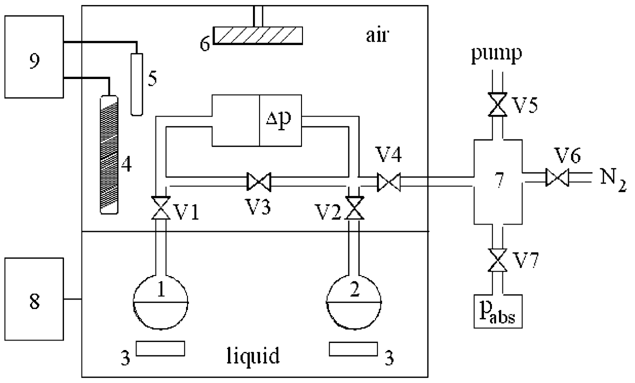

Figure 1. Scheme of the vapor pressure apparatus. 1 and 2, glass flasks with solution or pure solvent; 3, magnetic stirrer; 4, heater; 5, temperature sensor; 6, circulating ventilator; 7, buffer vessel; 8 and 9, control units; V1 to V7, valves.

2. Experimental Section

2.1. Apparatus. The apparatus is based on the principle of the precise vapor pressure measuring system built in our institute several years ago.[17] Its structure and main parts are shown in Figure 1. The apparatus consists of a liquid thermostat (Lauda UB 30J) surmounted by an air thermostat; the samples are immersed in the liquid with the differential pressure manometer (MKS Baratron, Type 616A01TRE) in the air above. To prevent condensation of the vapor, the temperature of the air thermostat is kept approximately 10 K higher than the liquid thermostat. For the absolute pressure measurement up to 133 kPa, an internally thermostated absolute pressure sensor (MKS Baratron, Type 690A.1TRC) positioned outside the air thermostat is used.

The differential manometer (Δp) has a maximum range of 133 Pa. If the pressure difference between solvent and solution is less than this maximum range, the differential pressure can directly be measured. In this case, flask 1 is filled with the solution and the reference pressure is the vapor pressure of the solvent in flask 2.

To measure higher pressure differences or absolute vapor pressures, the pure solvent or the solutions are filled in flask 1 and the pressure is compensated with nitrogen (via

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valves V4 and V7). The differential manometer then works only as a null device, and the total pressure is determined with the absolute manometer (p_{abs}). In this case, flask 2 is not used.

The liquid thermostat was calibrated with the help of a precision platinum resistance thermometer (F250, Automatic System laboratories, UK) with an uncertainty of $\sigma(T) = 10$ mK. Temperature fluctuations were less than 0.003 K. As a thermostat, fluid silicone oil (M50) for the temperature range (363 to 473) K and water for (278 to 363) K was used.

The air thermostat is essentially a stainless steel box with thermally isolated double walls, provided with some feedthroughs (electrical support, pipelines, valve handles etc.). The thermostat is controlled using a Pt100 thermosensor (5), a heater (4), and the control unit (9) from Heju Juchheim (LTR 4200). The temperature gradient inside the air thermostat, depending on the distance to the heater, does not exceed 4 K.

The internal pipeline system in the air thermostat connects the differential pressure sensor to the samples (via valves V1 and V2) and to the buffer vessel (V4). Valve V3 allows pressure equalization between both sides of the manometer necessary to adjust the zero point.

Valve V5 connects the apparatus to the vacuum system (molecular pump, Pfeiffer). The pipeline system consists of stainless steel pipes of 6 mm internal diameter, flask sockets, and valves (Swagelok). The valve handles are elongated and controlled from outside the air thermostat.

The stirring system uses AlNiCo (6 × 25 mm^2) magnets from IBS Magnet Company (magnet force stable up to 673 K), fixed to supporting plates, which are driven from outside by electric motors via specially manufactured flexible axles (Schmid & Wezel, Hilsbach).

2.2. Procedure and Degassing. Before putting the sample in the thermostat bath, it was necessary to degas the system and the sample thoroughly; otherwise, the dissolved gases will give rise to an apparent higher total pressure.[17] The samples were degassed by reflux under vacuum to avoid contact with air or moisture. The sample in the cell was further degassed by heating with constant stirring and allowing some evaporation to remove the last traces of air. After degassing, the cell was immersed in the liquid thermostat. The volume of the gas space was estimated to be 19 cm^3, leading to a maximum error of ±0.002% in the concentration by evaporation of the solvent and was therefore negligible. Starting at 298.15 K, the temperature was increased stepwise in 5-K increments. After the temperature was changed, a new equilibrium state (constant pressure) was obtained in approximately (30 to 45) min. After the vapor-pressure measurement, the solution compositions (in the case of electrolyte solutions) were determined by weighing the flask and determining the amount of solvent loss from the solution due to evaporation during the degassing procedure.

2.3. Chemicals. Water from the Millipore purification system with specific conductivity of less than 2×10^{-7} S·m^{-1} was used. Sodium chloride (Merck, GR, min 99.95%) was used without further purification and was dried in an electrical oven at about 393.15 K for 24 h prior to use.

The purity of the alcohols was checked with gas chromatography (HP-6890) with a flame ionization detector (FID). Impurities of ethanol (Merck, min 99.8%), 1-propanol (Merck, min 99.8%), 2-propanol (Merck, min 99.7%), and 1-butanol (Fluka, min 99.8%) were undetectable with GC. For methanol (Merck, min 99.8%) and 2-butanol (Merck, min 99.5%), a purity of 99.97% and 99.95% was determined with GC, respectively. The water content of all the alcohols by Karl Fischer titration (mci, model CA-02) was less than 0.013%, 0.01%, 0.014%, 0.057%, 0.025%, and 0.007% respectively for methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. All chemicals were used without further purifications.

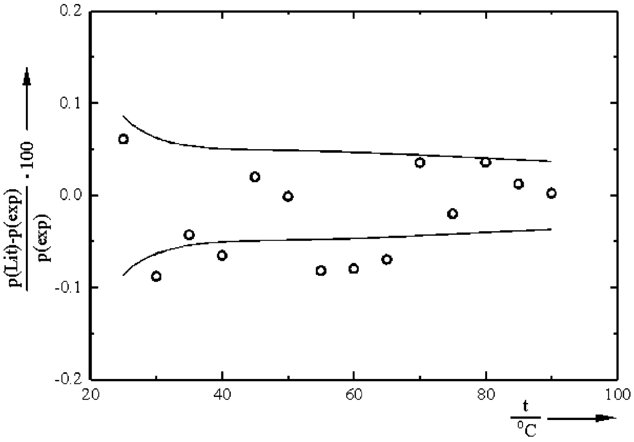

Figure 2. Comparison of measured water vapor pressures with Ambrose's and Lawrenson's data.[27] The lines correspond to fluctuation in temperature of 0.01 K.

Table 1. Experimental Vapor Pressures of Methanol and Comparison with Literature Data[a]

T/K	p/kPa	$100\Delta p/p^b$	$100\Delta p/p^c$	$100\Delta p/p^d$	$100\Delta p/p^e$
298.15	16.954	0.007	−0.003	0.016	−0.004
303.15	21.884	0.009	−0.001	0.014	−0.012
308.15	27.977	0.006	0.000	0.007	−0.006
313.15	35.510	0.025	0.016	0.023	0.023
318.15	44.585	0.009	0.000	0.004	0.006
323.15	55.646	0.019	0.012	0.012	0.019
328.15	68.940	0.031	0.018	0.022	
333.15	84.617	0.013	0.004	0.002	

[a] $\Delta p = p - p_{\mathrm{lit}}$. [b] Ambrose et al.[25] [c] Gibbard et al.[9] [d] Holldroff et al.[30] [e] Garriga et al.[31]

3. Results and Discussion

The temperature-dependent vapor pressure of water was measured to check the reliability and accuracy of the whole measuring system. The reason for selecting water is that very reliable data are available in the literature. Ambrose and Lawrenson[27] compared their data with many literature data and found the deviation less than 2 Pa up to 313.15 K and less than 5 Pa up to 373.15 K. The agreement between experimental values for water vapor pressure from (298.15 to 363.15) K and those reported by Ambrose et al.[27] and Saul et al.[28] is better than 0.1%, cf. Figure 2.

For a further check of our apparatus, we measured vapor pressures of pure methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. The results are reported in Tables 1−6, respectively, together with the deviation from literature $[\{(p - p_{\mathrm{lit}})\}/\{p\}] \times 100$.

The data are fitted with the Antoine equation

$$\ln(p/\mathrm{kPa}) = A - \frac{B}{(T/\mathrm{K} + C)} \qquad (1)$$

A, B, and C are adjustable parameters and can be found in Table 7.

For all studied alcohols, we compared the experimental data of this work with literature data in the appropriate temperature range.

Table 2. Experimental Vapor Pressures of Ethanol and Comparison with Literature Data[a]

T/K	p/kPa	$100\Delta p/p^b$	$100\Delta p/p^c$	$100\Delta p/p^d$	$100\Delta p/p^e$
298.15	7.916	0.071	0.077	0.083	0.120
303.15	10.542	0.100	0.084	0.013	0.130
308.15	13.841	0.082	0.072	0.017	0.100
313.15	17.982	0.058	0.019	0.001	0.067
318.15	23.169	0.049	0.059	0.036	0.054
323.15	29.579	0.038	0.090	0.072	0.043
328.15	37.456	0.035			0.040
333.15	46.955	0.007			0.012
338.15	58.580	0.020			0.026
343.15	72.243	−0.021			−0.015
348.15	88.655	−0.031			−0.026

[a] $\Delta p = p - p_{\text{lit}}$. [b] Ambrose et al.[32] [c] Garriga et al.[33] [d] Garriga et al.[34] [e] Antosik et al.[35]

Table 3. Experimental Vapor Pressures of 1-Propanol and Comparison with Literature Data[a]

T/K	p/kPa	$100\Delta p/p^b$	$100\Delta p/p^c$	$100\Delta p/p^d$
298.15	2.880			0.276
303.15	3.998		0.602	0.412
308.15	5.374		0.429	0.307
313.15	7.197		0.368	0.296
318.15	9.568		0.321	0.298
323.15	12.424		0.202	0.185
328.15	16.144		0.196	
333.15	20.718	0.281	0.152	
338.15	26.406	0.283	0.142	
343.15	33.226	0.232	0.080	
348.15	41.628	0.232	0.073	
353.15	51.670	0.215	0.048	
358.15	63.691	0.207	0.032	
363.15	77.812	0.178	−0.007	

[a] $\Delta p = p - p_{\text{lit}}$. [b] Ambrose et al.[32] [c] Dejoz et al.[36] [d] Munday et al.[11]

Table 4. Experimental Vapor Pressures of 2-Propanol and Comparison with Literature Data[a]

T/K	p/kPa	$100\Delta p/p^b$	$100\Delta p/p^c$
298.15	5.799		
303.15	7.859		0.006
308.15	10.521		−0.014
313.15	13.939		−0.014
318.15	18.240		−0.033
323.15	23.643		−0.040
328.15	30.346	0.012	−0.047
333.15	38.590	0.011	−0.054
338.15	48.659	0.016	−0.057
343.15	60.665	−0.016	−0.101
348.15	75.225	−0.011	−0.112
353.15	92.444	−0.022	−0.143

[a] $\Delta p = p - p_{\text{lit}}$. [b] Ambrose et al.[32] [c] Dejoz et al.[36]

Table 5. Experimental Vapor Pressures of 1-Butanol and Comparison with Literature Data[a]

T/K	p/kPa	$100\Delta p/p^b$	$100\Delta p/p^c$	$100\Delta p/p^d$	$100\Delta p/p^e$	$100\Delta p/p^f$
298.15	1.003			0.957	0.930	0.661
303.15	1.317			−0.181	0.022	−0.269
308.15	1.841			−0.099	0.103	−0.204
313.15	2.544			−0.006	0.135	−0.132
318.15	3.453		−0.025	0.090	0.094	−0.137
323.15	4.648		−0.031	0.109	0.178	−0.105
328.15	6.171		−0.061			
333.15	8.103		−0.089			
338.15	10.559		−0.077			
343.15	13.596		−0.091			
348.15	17.369		−0.086			
353.15	21.980	0.084	−0.088			
358.15	27.652	0.100	−0.057			
363.15	34.406	0.080	−0.066			

[a] $\Delta p = p - p_{\text{lit}}$. [b] Ambrose et al.[32] [c] Dejoz et al.[37] [d] Garriga et al.[38] [e] Garriga et al.[39] [f] Munday et al.[11]

Table 6. Experimental Vapor Pressure of 2-Butanol and Comparison with Literature Data[a]

T/K	p/kPa	$100\Delta p/p^b$	$100\Delta p/p^c$	$100\Delta p/p^d$	$100\Delta p/p^e$
298.15	2.440			0.735	0.637
303.15	3.373			0.183	0.464
308.15	4.588		0.020	0.431	0.367
313.15	6.234		0.043	0.402	0.398
318.15	8.252		−0.106	0.258	0.238
323.15	10.860		−0.172	0.172	0.189
328.15	14.133		−0.233		
333.15	18.337		−0.189		
338.15	23.487		−0.182		
343.15	29.706	0.058	−0.216		
348.15	37.202	0.001	−0.263		
353.15	46.358	−0.003	−0.262		
358.15	57.156	−0.034	−0.296		
363.15	70.237	−0.001	−0.271		

[a] $\Delta p = p - p_{\text{lit}}$. [b] Ambrose et al.[32] [c] Dejoz et al.[37] [d] Garriga et al.[39] [e] Garriga et al.[40]

Table 7. Constants of Antoine Equation $\ln(P/\text{kPa}) = A - B/(T/\text{K} + C)$ along with the Root-Mean-Square (rms) Deviations[a]

compound	temperature range/K	A	B	C	δ_{rms}/kPa
methanol	298−333	16.422	3544.452	−370.682	0.028
ethanol	298−348	16.402	3534.459	−51.570	0.031
1-propanol	298−363	16.089	3467.230	−68.020	0.021
2-propanol	298−353	15.976	3228.981	−71.116	0.024
1-butanol	298−363	16.473	3859.736	−64.740	0.022
2-butanol	298−363	15.779	3314.129	−75.653	0.043

[a] $\delta_{\text{rms}} = [\sum (p - p_{\text{calc}})^2/n]^{0.5}$, where n is the number of experimental data points.

(1) Concerning methanol, our results are in good agreement with data of Ambrose et al.,[25] Gibbard et al.,[9] Holldroff et al.,[30] and Garriga et al.[31] The agreement is best with the data given by Gibbard et al.,[9] which were obtained by a static method with a precision of ±0.002 K in temperature and ±0.66 Pa in pressure.

(2) In the case of ethanol, our results are in agreement with the literature data, although our results are slightly higher than literature data except two data points given in the paper of Ambrose et al.[32] and two others given by Antosik et al.;[35] see Table 2. The temperature range of the data of Garriga et al.[33,34] is only from (298.15 to 323.15) K. There is obviously a mistake in Table 1 of the paper of Antosik et al.[35] The column for ethanol and water seem to be exchanged.

(3) In the case of 1-propanol and 2-propanol, literature data for the whole temperature range of our study are rare. For 1-propanol, for temperatures lower than 323.15 K, the agreement of our data is better with Munday et al.[11] but all of our data were higher than those reported by Ambrose et al.,[32] Dejoz et al. (without one data point),[36] and Munday et al.[11] In 2-propanol, all of the compared data are lower than our measurements except for 3 values of Ambrose et al.[32] and one value of Dejoz et al.[36]

(4) Concerning 1-butanol and 2-butanol, precise temperature-dependent literature data are also rare. For 1-butanol, the data of Dejoz et al.[37] is in better agreement with our measurements, but all their indicated values are lower than the data we determined. For 2-butanol, for temperatures higher than 343.15 K the agreement is better with the data given by Ambrose et al.[32]

The Clausius−Clapeyron equation is a general equation originally relating vapor pressure, temperature, volume change, and enthalpy of vaporization of a pure liquid in

Table 8. Comparison of the Enthalpy of Vaporization Values for the Studies Alcohols with Calorimetric Values[a] at 298.15 K

compound	$\Delta_{vap}H$/kJ·mol^{-1}	$\delta\Delta_{vap}H^{b,c}$	$\delta\Delta_{vap}H^{b,d}$
methanol	37.965	0.01%	1.17%
ethanol	41.680	1.12%	1.05%
1-propanol	45.721	1.88%	0.11%
2-propanol	43.988	2.72%	1.69%
1-butanol	48.397	*e*	−0.34%
2-butanol	46.219	1.44%	−3.91%

[a] Majer and Svoboda.[41] [b] $\delta\Delta_{vap}H = (\Delta_{vap}H - \Delta_{vap}H_{cal})100/\Delta_{vap}H_{cal}$. [c] Ambrose et al.[32] [d] This work. [e] Not sufficient number of data in the measured range.

equilibrium with the gas phase. If the volume of the liquid is much smaller than that of the gas and therefore is neglected and the gas-phase behavior is treated as ideal, then the Clausius−Clapeyron equation becomes

$$\frac{d(\ln(p))}{d(1/T)} = \frac{-\Delta_{vap}H}{R} \tag{2}$$

where p is the vapor pressure, $\Delta_{vap}H$ is the enthalpy of vaporization, T is the absolute temperature, and R is the gas constant. A linear relationship between ln(p) and 1/T as we found in our measurements shows that the enthalpy of vaporization is temperature independent over the temperature range studied. These values for the studied alcohols are given in Table 8, together with a comparison with calorimetric values[41] at 298.15 K. It can be seen that the overall precision is comparable for Ambrose's and our data. Since the enthalpies of vaporization in ref 41 are determined in a different way, it is difficult to explain the origin of the differences in both techniques.

The final purpose of our new apparatus is the measurement of osmotic coefficients of electrolyte solutions over a wide temperature range. As a further check of our equipment, we therefore measured the vapor pressures of aqueous NaCl solutions from (298.15 to 363.15) K in 5-K intervals and at three compositions corresponding to molalities between (1 and 4) mol·kg^{-1}. The salt was not volatile so that the total measured pressure at equilibrium p is the vapor pressure of water. Osmotic coefficients for the solution of NaCl in water as a function of molality m were calculated from the measured pressures p using the following relations

$$\phi = -\frac{\ln a_w}{\nu m M_s} \tag{3}$$

$$\ln a_w = \ln\left(\frac{p}{p^*}\right) + \frac{(B_s - V_s^*)(p - p^*)}{RT} \tag{4}$$

In these equations a_w is the activity of the solvent, ν is the stoichiometric number of the salt, M_s is the molecular weight of the solvent, T is the absolute temperature, p is the vapor pressure of the solution, and p^* is that of the pure solvent. B_s is the second virial coefficient, and V_s^* is the molar volume of pure solvent. The second term on the right-hand side of eq 4 is the correction for nonideality of the solvent vapor through the virial equation. The second virial coefficient[42] and the molar volumes of pure water[43] from (298.15 to 363.15) K are given in Table 9.

We have reported in Table 10 our experimental vapor-pressure data, the corresponding values of the activity of water a_w, and the osmotic coefficients. For calculation of a_w, our experimental vapor-pressure data of pure water were used.

Table 9. The Second Virial Coefficient and Molar Volume of Pure Water at Different Temperatures

T/K	$10^4 B_s{}^a$/m^3·mol^{-1}	$10^6 V_s{}^{*b}$/m^3·mol^{-1}
298.15	−12.369	18.069
303.15	−11.373	18.094
308.15	−10.489	18.124
313.15	−9.701	18.157
318.15	−8.997	18.193
323.15	−8.367	18.234
328.15	−7.800	18.277
333.15	−7.290	18.323
338.15	−6.828	18.373
343.15	−6.410	18.425
348.15	−6.030	18.480
353.15	−5.684	18.538
358.15	−5.368	18.599
363.15	−5.078	18.663

[a] Poling et al.[42] [b] Keenan et al.[43]

Table 10. Measured Vapor Pressure of Aqueous Sodium Chloride Solution, p, at the Equilibrium Temperature, T, Calculated Values of the Activity of Water in the Liquid Phase, a_w, and the Osmotic Coefficient, ϕ, at Different Molalities m

T/K	p/kPa	a_w	ϕ	T/K	p/kPa	a_w	ϕ
m = 1.0684 mol·kg^{-1}							
298.15	3.046	0.9646	0.9370	333.15	19.208	0.9638	0.9591
303.15	4.106	0.9630	0.9795	338.15	24.136	0.9646	0.9369
308.15	5.421	0.9623	0.9996	343.15	30.058	0.9642	0.9459
313.15	7.110	0.9628	0.9839	348.15	37.171	0.9642	0.9480
318.15	9.244	0.9642	0.9470	353.15	45.599	0.9630	0.9789
323.15	11.89	0.9644	0.9415	358.15	55.691	0.9633	0.9724
328.15	15.177	0.9635	0.9647	363.15	67.590	0.9640	0.9520
m = 2.1950 mol·kg^{-1}							
298.15	2.929	0.9245	0.9931	333.15	18.387	0.9227	1.0172
303.15	3.918	0.9230	1.0125	338.15	23.111	0.9239	1.0013
308.15	5.191	0.9227	1.0168	343.15	28.799	0.9241	0.9987
313.15	6.810	0.9228	1.0165	348.15	35.583	0.9231	1.0121
318.15	8.839	0.9226	1.0183	353.15	43.726	0.9234	1.0074
323.15	11.404	0.9240	0.9997	358.15	53.360	0.9234	1.0075
328.15	14.562	0.9247	0.9904	363.15	64.752	0.9240	0.9993
m = 3.5714 mol·kg^{-1}							
298.15	2.739	0.8688	1.0927	333.15	17.292	0.8679	1.1009
303.15	3.676	0.8661	1.1170	338.15	21.693	0.8674	1.1058
308.15	4.862	0.8676	1.1035	343.15	27.028	0.8675	1.1049
313.15	6.401	0.8674	1.1051	348.15	33.429	0.8675	1.1049
318.15	8.325	0.8684	1.0970	353.15	41.133	0.8689	1.0916
323.15	10.710	0.8679	1.1014	358.15	50.155	0.8683	1.0976
328.15	13.676	0.8686	1.0951	363.15	60.855	0.8688	1.0932

Table 11. Comparison between Experimental Osmotic Coefficient Values, ϕ, and Those Proposed by Gibbard et al.,[8] ϕ_{ref}, and Corresponding Deviation in Osmotic Coefficient and Vapor Pressure at Different Molalities

T/K	ϕ	ϕ_{ref}	$\Delta\phi$	$100(\Delta p/p)^a$
m = 1.0684 mol·kg^{-1}				
298.15	0.9370	0.9390	0.0020	0.007
323.15	0.9415	0.9434	0.0019	0.007
348.15	0.9480	0.9433	0.0047	0.018
m = 2.1950 mol·kg^{-1}				
298.15	0.9931	0.9945	0.0014	0.011
323.15	0.9997	1.0077	0.0080	0.063
348.15	1.0121	1.0047	0.0074	0.059
m = 3.5714 mol·kg^{-1}				
298.15	1.0927	1.0812	0.0115	0.148
323.15	1.1014	1.0897	0.0117	0.151
348.15	1.1049	1.0881	0.0168	0.216

[a] $\Delta p = p_{ref} - p$.

Table 11 shows the comparison between experimental osmotic coefficient values, ϕ, and those proposed by Gibbard et al.,[8] ϕ_{ref}. At each temperature, the experimental data of

Gibbard et al.[8] were regressed using a polynomial expression in molality. From the deviation in the osmotic coefficients, the corresponding deviation of the vapor pressure was calculated at different molalities m using the following relations

$$\Delta\phi = |\phi_{\text{ref}} - \phi| \tag{5}$$

$$\frac{\Delta p}{p} = \left(\frac{p_{\text{ref}} - p}{p}\right) = \frac{\upsilon M_{\text{s}} m \Delta\phi}{1000} \tag{6}$$

according to the expression

$$\Delta\phi \cong \frac{1000}{\nu M_{\text{w}} m}\frac{\Delta p}{p} \tag{7}$$

Note that a very small deviation in vapor pressure can lead to a large deviation in the osmotic coefficient, when the molality tends to zero.

The overall agreement between our data and the data of Gibbard et al.[8] is very satisfactory. For the lower concentrations, the deviations in the osmotic coefficients are around 0.5%, whereas at the concentrations higher than 3 mol·kg^{-1}, they are up to 1.5%. The deviations also increase slightly with temperature.

4. Conclusions

An apparatus has been constructed for measuring the vapor pressure of pure compounds and liquid solutions. Systems may be measured from (278 to 473) K with an overall uncertainty in temperature of $\sigma(T) = 0.003$ K and in pressure lower than $\sigma(p) = 0.01\%$ of reading and a maximum $\sigma(c) = \pm 4 \times 10^{-5}$ mol·kg^{-1} in the concentration. The vapor pressures of pure water and aqueous solution of NaCl were measured and compared with literature. For better checking of the apparatus, the measured vapor pressures of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol are compared with literature data. In all cases, the agreement with literature data is very satisfactory so that it can be expected that the apparatus can be used with confidence for the determination of temperature-dependent osmotic coefficients of aqueous and nonaqueous electrolyte solutions.

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