III were calculated in the conventional way from values of $E°(M) - E°(Fc)$. On the basis of both assumptions, chloride ion is, as expected, considerably more solvated in methanol than in propylene carbonate. For anions with a localized charge this is primarily due to hydrogen bonding of the alcohol to these anions. Ion–dipole interaction between the anion and an aprotic solvent is impeded by steric shielding of the positive end of the dipole in many aprotic solvents. On the other hand, when the charge is highly delocalized, as in the lipophilic picrate ion, a negligible free energy of transfer has been found between methanol and aprotic solvents (*5*), PC being a typical aprotic solvent. It is of interest to report the transfer activity coefficient of M^+ (except, of course, Ag^+) between the two aprotic solvents AN and PC. Values of $\log {}^{AN}\gamma^{PC}(M^+)$ are −0.1, +0.6, +0.2, +0.1, +0.1, and +0.1 for Li^+, Na^+, K^+, Rb^+, Cs^+, and Tl^+.

Considering the Born effect, which attempts to take into account the solvent's dielectric constant, the values of $\log {}^{AN}\gamma^{PC}(M^+)$ become +2.5, +2.2, +1.3, +1.1, +1.0, and +1.1, respectively, while those of $\log {}^{M}\gamma^{PC}(M^+)$ become +3.5, +1.2, $+0.7_4$, $+0.4_2$, +1.3, and +4.0. In the latter series M^+ is Na^+, K^+, Rb^+, Cs^+, Tl^+, and Ag^+. Dielectric constants (*23*) of 32.7, 36.0, and 64.4 of M, AN, and PC, respectively, and Pauling's (*24*) crystallographic radii were used. It appears that, corrected for the Born effect, all the alkali ions and Tl^+, particularly Li^+ and Na^+, are considerably more solvated in M or AN than in PC. This is the opposite of what would be expected on the basis of ion–dipole interaction, the dipole moments (*23*) of PC, AN, and M being 4.98, 3.92, and 1.70 D, respectively. Evidently, nonelectric (neutral) ion–solvent interactions play an important role.

The species $AgCl_2^-$ is solvated to about the same extent in nitromethane, sulfolane, and dimethyl sulfoxide as in PC but is solvated to a greater extent in M and AN. In the order given, values of $\log {}^{PC}\gamma^{S}(AgCl_2^-)$ are +0.2 (*25*), -0.8 (*26*), +0.2, +1.9, and +1.9. As compared to Ag^+ and Cl^-, which are hydrophilic, $AgCl_2^-$ has considerable lipophilic character and is a soft anion as compared to the hard chloride ion, $\log {}^{PC}\gamma^{M}(AgCl_2^-) - \log {}^{PC}\gamma^{M}(Cl^-)$ being 1.9 + 4.1 = 6.0. As a matter of fact, $AgCl_2^-$ appears to be more lipophilic than the picrate ion, $\log {}^{PC}\gamma^{M}(Pi^-)$ being +0.3 as compared to $\log {}^{PC}\gamma^{M}(AgCl_2^-)$ of +1.9. The difference between $\log \gamma$ values of two ions is independent of the assumption on which γ values are based.

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Mutual Diffusion Coefficients of $BaCl_2$–H_2O and KCl–H_2O at 25 °C from Rayleigh Interferometry

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The volume-fixed mutual diffusion coefficients of $BaCl_2$–H_2O and KCl–H_2O have been measured to an accuracy of 0.1–0.2%, from dilute solutions to near saturation, using free-diffusion Rayleigh interferometry. These diffusion coefficients are compared to other available diffusion data for these systems, measured by the conductometric and optical methods. The new data extend previously available optical results to higher and lower concentrations and confirm that the diffusion coefficients of $BaCl_2$–H_2O are unusually low, relative to the other alkaline earth chlorides, at moderate and high concentrations. The effect of cation hydration on the diffusion coefficients of alkali and alkaline earth chloride solutions is briefly discussed.

Introduction

Mixing of chemical species by diffusion is important in a variety of natural phenomena including some geochemical processes.[1] To understand these phenomena requires the use of accurate diffusion coefficient data. Although determinations of differential mutual diffusion coefficients have been made since the late 1940's, accurate diffusion data are available for relatively few systems. One reason for the scarcity of such data involves the large amount of effort involved in performing the experiments and, for optical methods, in the subsequent reading of the photographic records.

To supplement the available diffusion coefficient data, it is desirable to develop methods of approximating data for binary and for mixed salt systems. Very accurate data are required for a number of representative systems in order to correlate the diffusion coefficient with ionic radius, charge type, or other parameters. Diffusion data are already available for several alkali and alkaline earth chlorides at 25 °C, so they should be good choices for testing such correlations.

Accurate diffusion data are available for $CaCl_2$–H_2O,[2-4] $MgCl_2$–H_2O,[5,6] and $SrCl_2$–H_2O.[7,8] $BaCl_2$–H_2O has been studied by Harned's conductometric method at low concentrations[5] and Gouy interferometry[9] at higher concentrations. The diffusion coefficients of $BaCl_2$–H_2O seem to be anomalously low at moderate and high concentrations compared to the other alkaline earth chlorides, and the maximum in the diffusion curve seems to be unusually flat and broad. The agreement between data from this laboratory and Lyons' laboratory has generally been good.[4] However, the behavior of the $BaCl_2$–H_2O diffusion coefficients is sufficiently anomalous that additional measurements are desirable to verify that this unexpected behavior is real and to more accurately describe the shape of the diffusion curve at moderate and high concentrations.

A larger amount of data are available for alkali chlorides,[3,4,8-24] and the NaCl–H_2O system has recently been considered in detail.[4] The KCl–H_2O system has been the most thoroughly studied,[10-19] but gaps are present in the optical data at high and low concentrations. Consequently, some additional measurements are desirable for this salt.

In this present paper diffusion coefficients for $BaCl_2$–H_2O and KCl–H_2O are reported at 25 °C from dilute solutions to near saturation. These data extend available optical data to higher and lower concentrations than were previously studied. Data for most of the remaining alkali and alkaline earth chlorides are also being measured to provide an accurate data base for testing methods of estimating diffusion coefficients.

Experimental Section

The experimental details and methods of calculation are the same as in the earlier studies.[4,25] The diffusion coefficients for dilute solutions were corrected for their concentration dependence and for the concentration dependence of the refractive index. The diffusion coefficients are for the volume-fixed reference frame and were measured at 25.00 ± 0.005 °C. Most of the diffusion coefficients were measured in the Ta metal and glass cell that had been used for several earlier experiments.[25] Ta metal was chosen because it is extremely resistant to corrosion by most electrolyte solutions. The front and back windows of the cell are 1.0 cm thick optical flats. The Rayleigh mask is directly attached to the front of the cell, and the mask also serves to clamp the front window of the cell in place. The cell windows can easily be removed for cleaning. The other experiments were performed in the modified Beckman cell used for most of the earlier work.[4,25]

The mounts for the camera lens, the cylinder lens, and the focusing mirror were replaced at the beginning of the present study. The new mounts had built-in vernier scales or feeler gauges to facilitate adjustment of the optics of the diffusiometer. The optical alignment procedure was similar to the procedure briefly described in the NaCl–H_2O and $CaCl_2$–H_2O paper.[4] Magnification factors for the various cells in this realigned instrument increased by 0.65% from the previous alignment;[25] these larger values of MF are due to repositioning of the lenses. These magnification factors were determined by photographing a ruled scale in the center of cell position. The spacing between the Rayleigh fringes on the photographic plates increased from about 440 μm to about 450 μm due to this new alignment.

KCl solutions were prepared as previously described.[4] The $BaCl_2$ stock solution was prepared from recrystallized and filtered "Baker Analyzed" $BaCl_2 \cdot 2H_2O$. The claimed impurities of the starting material are 0.02% Ca, 0.01% Sr, 0.0002% heavy metals (as lead), and 0.0001% Fe. A sample of the $BaCl_2$ stock solution was evaporated to dryness and then analyzed by direct current arc optical emission spectroscopy. The approximate amounts of impurities by weight were 0.05% Sr, 0.002% Ca, 0.0001% Fe, 0.0003% Cu, 0.003% Al, 0.005% Si, and less than 0.001% Na and Mg.

Table I. Diffusion Coefficients of Aqueous $BaCl_2$ Solutions at 25 °C

$\bar{c}$	Δc	$m(\bar{c})$	J	$10^5 D_V$, $cm^2\ s^{-1}$	$10^5 M$, $cm^2\ s^{-1}$
0.004 443	0.008 886	0.004 457	26.37	1.262_1	1.399
0.007 037	0.014 074	0.007 059	41.43	1.246_0	1.405
0.009 192	0.018 384	0.009 221	53.99	1.236_5	1.410
0.013 153	0.026 305	0.013 196	77.05	1.222_7	1.414
0.018 530	0.027 890	0.018 593	81.21	1.208_8	1.417
0.026 584	0.025 024	0.026 680	72.69	1.195_5	1.420
0.043 989	0.028 047	0.044 168	81.01	1.179_8	1.419
0.071 862	0.027 742	0.072 206	79.55	1.168_1	1.414
0.121 84	0.028 50	0.122 59	80.97	1.156_5	1.394
0.184 90	0.029 41	0.186 35	82.56	1.151_1	1.369
0.302 36	0.030 10	0.305 78	83.13	1.150_7	1.324
0.389 81[a]	0.034 73	0.395 25	92.69	1.150_8	1.289
0.487 45	0.036 51	0.495 73	99.78	1.157_0	1.254
0.556 66[b]	0.027 94	0.567 35	74.36	1.158_6	1.227
0.634 31	0.042 29	0.648 10	113.57	1.160_4	1.195
0.807 22	0.039 29	0.829 49	104.73	1.167_8	1.130
0.999 28	0.037 74	1.033 6	98.69	1.174_1	1.062
1.208 2	0.034 78	1.259 1	90.51	1.180_8	0.998
1.610 7	0.053 17	1.704 0	134.33	1.168_0	0.890

[a] This solution pair was prepared directly from anhydrous $BaCl_2$.
[b] This experiment was performed in the modified Beckman cell, all other experiments were performed in the Ta cell.

The concentration of the $BaCl_2$ stock solution was determined by dehydration of triplicate samples of the stock solution at 150 °C after adding HCl to reduce hydrolysis during drying; 1.4619 ± 0.0002 mol kg^{-1} was obtained. In addition, triplicate sulfate analysis yielded 1.4624 ± 0.0002 mol kg^{-1}; the average of these two sets of analyses was used in the concentration calculations. The highest concentration pair was obtained by evaporation of H_2O from weighed samples of the stock solution. All but one $BaCl_2$–H_2O experiment was performed with solutions prepared from the stock solution. The other experiment was done with samples prepared directly from oven dried $BaCl_2$.

The molecular weights used were 208.236 g mol^{-1} for $BaCl_2$, 233.39 g mol^{-1} for $BaSO_4$, and 74.551 g mol^{-1} for KCl. All dilutions were prepared by weight, and all weights were converted to mass.

Previous measurements with our diffusiometer and realigned optics indicated an accuracy of 0.1–0.2% for the diffusion coefficients. The double pass optical arrangement of our diffusiometer allows fairly low concentrations to be studied, with enough Rayleigh fringes being available for good statistical averaging. A second advantage of the double pass arrangement is that data may be obtained closer to saturation than is possible for single pass optics, since smaller concentration differences can be used in the experiments.

The experimental diffusion data are given in Tables I and II. The total number of Rayleigh fringes is denoted by J, the volume-fixed diffusion coefficient by D_v, the average molar concentration of the pair of diffusing solutions in units of mol dm^{-3} by $\bar{c}$, the concentration difference across the boundary by Δc, and the molal concentration corresponding to $\bar{c}$ by $m(\bar{c})$.

Values of $J/\Delta c$, related to the refractive index gradient, exhibit slightly larger scatter for runs with the Ta cell compared to earlier runs in the modified Beckman cell. This appears to be due, at least in part, to slight differences that occur in the cell depth after it has been dismantled for cleaning and then reassembled. Such differences do not affect the values of D_v because all effects of cell thickness cancel in Rayleigh experiments (although not for Gouy measurements).

Some of the scatter in $J/\Delta c$ for $BaCl_2$–H_2O at intermediate and high concentrations could also have originated in errors for

Table II. Diffusion Coefficients of Aqueous KCl Solutions at 25 °C

$\bar{c}$	Δc	$m(\bar{c})$	J	$10^5 D_V$, $cm^2\ s^{-1}$	$10^5 M$, $cm^2\ s^{-1}$
0.013 599	0.027 198	0.013 645	26.19	1.901_7	2.006
0.022 495	0.044 989	0.022 575	43.36	1.885_0	2.009
0.088 540	0.077 576	0.089 018	73.52	1.853_3	2.039
0.099 317[a]	0.099 158	0.099 884	91.77	1.847_7	2.038
0.158 59	0.098 72	0.159 76	92.56	1.838_2	2.046
0.206 83[a]	0.098 45	0.208 64	89.97	1.837_9	2.054
0.274 85	0.104 03	0.277 80	96.06	1.837_6	2.061
0.731 56	0.095 30	0.749 37	84.89	1.868_4	2.086
0.999 28[a, b]	0.118 42	1.032 0	100.87	1.891_8	2.091
1.248 4	0.101 1	1.299 3	86.71	1.915_8	2.092
1.610 1	0.103 3	1.695 2	86.76	1.959_1	2.095
2.101 3	0.104 1	2.248 6	85.24	2.013_6	2.082
2.347 9	0.086 9	2.533 8	69.29	2.037_1	2.068
2.634 8	0.075 7	2.871 8	59.75	2.069_0	2.054
2.875 5[a]	0.085 8	3.160 8	66.13	2.096_2	2.040
3.231 4	0.096 9	3.597 8	74.93	2.132_5	2.014
3.900 4[a, b]	0.121 5	4.452 3	88.03	2.196_1	1.959
4.045 9[a]	0.076 8	4.644 2	56.93	2.208_8	1.946

[a] These experiments were performed in the modified Beckman cell, the other experiments were performed in the Ta cell. [b] These two experiments were performed by L. B. Eppstein in this laboratory.

Table III. Polynomial Coefficients for the Density Equations

A_i	KCl[a]		$BaCl_2$[b]	
A_2	0.047422	0.047630	0.183802	0.184891
A_3	−0.0010978	−0.0013583	−0.00526062	−0.00696335
A_4	−0.0022142	−0.00059647	−0.00619260	0.0
A_5	0.00030692	0.00011744	0.0	0.0
std dev	0.00001	0.00001	0.00003	0.00003
max concn	4.806	4.168	1.7843	1.6820
concn scale	molality	molarity	molality	molarity

[a] 130 points were given nonzero weights in the least-squares fits for this salt. The maximum concentration is the saturated solution. [b] 57 points were given nonzero weights in the least-squares fits for this salt. The maximum concentration is the saturated solution.

Δc of 0.0003 mol dm^{-3} (0.00015 mol dm^{-3} in $\bar{c}$). The largest deviation from the $J/\Delta c$ curve occurred for the solution pair prepared from the anhydrous salt; this is probably a less accurate method of solution preparation (the solution became quite hot when H_2O was added to the anhydrous $BaCl_2$).

Results and Discussion

The solutions were prepared by weight, and density data are required to interconvert the molality and molarity concentration scales. Available density data for $BaCl_2$–H_2O[26-35] were fitted to least-squares equations of the form

$$d = d_0 + \sum_{i=2}^{n} A_i X^{i/2} \qquad (1)$$

where $X = c$ or m.

These densities were normalized to d_0 = 0.997 045 g cm^{-3} for pure water[36] and were converted to the molecular weights used in this study. The coefficients and standard deviations for eq 1 are given in Table III. Density coefficients presented earlier[4] for KCl–H_2O are also included but have been converted from grams per milliliter to grams per cubic centimeter.

The various sets of $BaCl_2$ density data were given weights for the least-squares equations based on their internal consistency and upon agreement with other studies. Herz and Hiebenthal[28] and Vasilëv et al.[33] were given zero weights because of systematic differences from the other available data; Jones and Dole's data[29] were given zero weights because of large scatter. The other density data were given weights of 1.0,[31,32,34] 0.75,[26,30] or 0.5.[27] The data of Millero et al.[35] were weighted 1.0 up to 0.6 mol kg^{-1} and 0.5 at higher concentrations.

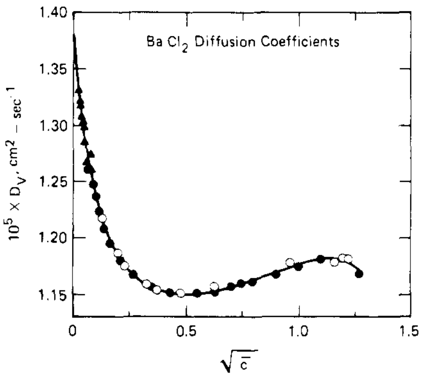

Figure 1. The diffusion coefficients of $BaCl_2$ solutions at 25 °C as a function of the square root of the molarity: ▲, Harned and Polestra;[5] ○, Vitagliano and Lyons;[9] ●, this research.

Table I contains the experimental $BaCl_2$–H_2O diffusion data, and Figure 1 compares the available data graphically. The present $BaCl_2$–H_2O diffusion data connect up smoothly with Harned and Polestra's conductometric values[5] and are in good agreement with Vitagliano and Lyons' Gouy results.[9] The maximum difference between the Gouy and Rayleigh studies is 0.5%, with most of the points within 0.2–0.3%. Vitagliano and Lyons' two lowest concentration values are 0.4–0.5% high. As noted by these authors, conventional averaging procedures ordinarily give high values for D_v for the skewed Gouy patterns of dilute electrolyte solutions, so at least part of this difference arises from this source. Because of this computational problem, extrapolation of the Gouy results to lower concentrations can result in errors as large as 0.7% for this salt. The combined data for $BaCl_2$–H_2O indicate that the diffusion coefficients go through a maximum, and this is typical of chloride salts that are sufficiently soluble. The basic trend in D_v as a function of concentration is close to that found by Vitagliano and Lyons,[9] but the shape of the diffusion curve is now more accurately characterized.

The thermodynamic diffusion coefficients, M, for $BaCl_2$–H_2O are also given in Table I and were calculated from the equation

$$M = D_v/(d(m\Phi)/dm) \qquad (2)$$

where Φ is the osmotic coefficient. Activity derivatives were obtained by differentiation of the osmotic coefficient equation

$$\Phi = 1 - (A/3)m^{1/2} + \sum_i A_i m_i^{r_i} \qquad (3)$$

where A = 4.0744 is the Debye–Hückel limiting slope. Values of A_i and r_i were obtained by least-squares fits of available isopiestic[37-39] and freezing point depression data.[40] The review of Goldberg and Nuttall[41] indicated that these data are the most consistent for this salt, and references to other less accurate activity data can be found in their article.

The osmotic coefficients of $BaCl_2$–H_2O from isopiestic data were calculated by using Hamer and Wu's results for the KCl and NaCl isopiestic standards.[42] Freezing point depression data were converted to osmotic coefficients at 25 °C by using available heat of dilution[43] and heat capacity[44] results. The parameters for eq 3 and the standard deviation of the best fit are given in Table IV.

Freezing-point depression data[40] above 0.39 mol kg^{-1} were not included in the least-squares calculations since the heat capacity results[44] only extend to this concentration. The various activity data were given unit weights except for a few outlying

Table IV. Coefficients and Powers for the Osmotic Coefficient Polynomial for $BaCl_2$

i	r_i	A_i
1	0.75	−0.3829360
2	1.00	9.515497
3	1.25	−16.56763
4	1.50	11.82468
5	1.75	−3.096269
std dev		0.0016
max concn		1.788 mol kg^{-1}

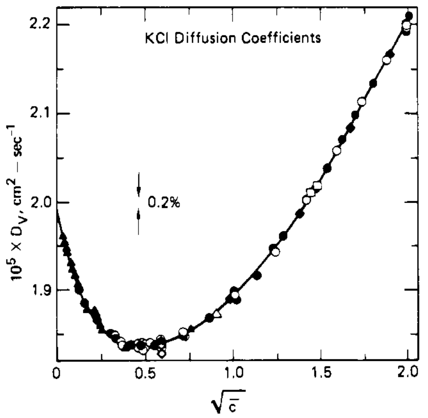

Figure 2. The diffusion coefficients of KCl solutions at 25 °C as a function of the square root of the molarity: ▲, Harned and co-workers;[10–12] ○, Gosting and co-workers;[13–15] ◇, Riley and Lyons;[16] ◆, Longsworth;[17] △, Cussler and Dunlop;[18] □, Chapman;[19] ●, this laboratory[4,25] including the present study.

points that were given zero weight.

The experimental diffusion data for $KCl-H_2O$ are given in Table II. Ten other points from this laboratory have already been published for this system.[4,25] Together these results constitute a thorough reinvestigation of this system. The values of M in Table II were calculated by differentiating Hamer and Wu's equation.[42] The activity derivatives could be uncertain by as much as 1.0% above 1.0 mol kg^{-1}. The available diffusion data for $KCl-H_2O$ are illustrated in Figure 2.

Diffusion data from the various optical measurements for $KCl-H_2O$ are in very good agreement with each other. None of the points deviates more than 0.3% from a smooth curve drawn through all of the available data, and none of the data from this laboratory deviates more than 0.2% from this curve. The conductometric results[10–12] have a larger scatter, about 0.4% at moderate concentrations, but are otherwise in complete agreement with the present results.

The $KCl-H_2O$ system provides an excellent comparison between the various experimental methods since accurate data have been measured by Harned's restricted diffusion conductometric method,[10–12] free diffusion Gouy interferometry,[13–18,18] restricted-diffusion Rayleigh interferometry,[19] and free-diffusion Rayleigh interferometry[4,17,25] (including present results). However, results obtained by differentiating integral diffusion data from diaphragm cell measurements are about 1% low at moderate concentrations.[45] This is probably due to differentiation errors rather than experimental error. Polarization interferometry results are only good to about 1–2%.[46]

The ionic radii of the alkali and alkaline earth ions increase with increasing atomic number.[47] The lower charge to radius ratio for the heavier ions should result in weaker hydration for the heavier ions compared to the lighter ions of the same charge type. This should result in higher water activities and lower osmotic coefficients with increasing atomic number since less water is tied up by ionic hydration. Cation hydration numbers calculated from activity coefficient data for the chloride salts decrease regularly with atomic number for these two series.[48] Decreased cation hydration should result in increased diffusion rates since the larger (free) ions would have smaller hydrated radii. The alkali and alkaline earth chloride osmotic and diffusion coefficients are consistent with these ideas, except for the diffusion coefficients of $BaCl_2-H_2O$ at moderate and high concentrations.

The osmotic coefficients of $BaCl_2-H_2O$ are lower than those for the other alkaline earth chlorides at all concentrations, while the D_v values are lower (except for $MgCl_2-H_2O$) at moderate and high concentrations. This anomalous behavior for $BaCl_2-H_2O$ does not occur for the thermodynamic diffusion coefficients M. That is, the M values of the alkaline earth chlorides are a more regular function of cation radius than are the D_v values. Although increased amounts of ion pairing for the heavy alkaline earth chlorides could be contributing to these effects, Robinson's isopiestic study[37] of $KCl-BaCl_2$ mixtures suggests that ionic association is weak in $BaCl_2-H_2O$ solutions.

It has been noted that ionic association can produce low diffusion coefficients[25] and even cause D_v to decrease regularly with increasing concentration. However, extensively self-complexed salts like CdI_2 still have maxima and minima in D_v;[49] consequently the effect of ionic association on diffusion can vary significantly from case to case. One major difference between these two systems is that negative-charged complexes can form between Cd^{2+} and I^-,[50] while only ion pairs, such as hydrated $BaCl^+$, form in the alkaline earth chloride solutions.[51]

Acknowledgment

The authors are grateful to Professor John G. Albright for calculating some of the dilute solution corrections for D_v.

Glossary

D_v	mutual diffusion coefficient
Φ	molal osmotic coefficient
m	molal concentration of the solute
c	molar concentration of the solute
M	thermodynamic diffusion coefficient
d	density

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Vapor–Liquid Equilibrium Data for the Systems Acetone–Methanol and Methanol–Benzene in the Presence of Dissolved Salts

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The vapor–liquid equilibrium data at 760 mmHg pressure have been determined experimentally for the two binary systems, viz., acetone–methanol saturated with cadmium acetate and methanol–benzene saturated with magnesium acetate. The data obtained by using a Smith and Bonner type of equilibrium still were found to be thermodynamically consistent.

The advantages of using a salt as a separating agent in extractive distillation have been discussed by a few investigators (*2–5*). It has also been shown that a few systems, both aqueous and nonaqueous, exhibit departure from the general theory of salt effect in vapor–liquid equilibrium (*3*, *12–15*), vis., the presence of a dissolved salt would result in an increase in concentration in the equilibrium vapor of the component in which the salt was less soluble, due to the lowering of the vapor pressure of the other component in which it is more soluble. This work presents the isobaric vapor–liquid equilibrium data for two nonaqueous binary systems: (i) acetone–methanol saturated with cadmium acetate and (ii) methanol–benzene saturated with magnesium acetate. Both the salts were found to be soluble in methanol and only very sparingly soluble in the other components. The nonaqueous systems have been chosen in this work for the reason that these have not been studied for the effect of salt to the extent the aqueous systems have been investigated (*6*, *7*).

Experimental Section

The vapor–liquid equilibrium data were determined in a Smith and Bonner type of still with an arrangement for magnetic stirring the description of which is given elsewhere (*16–18*). The experimental technique and procedure were the same as outlined in earlier papers of one of the authors (*14*, *15*) excepting for the modification in the liquid composition estimation method. In this investigation, the liquid-phase composition was determined at the end of the run by evaporating to dryness the liquid mixture and then analyzing the condensate for composition by the density measurement at 30 ± 0.05 °C. The equilibrium data were determined at atmospheric pressure which remained constant in the range 760 ± 3 mmHg. To ensure saturation of the boiling liquid mixture with salt, the latter was added slightly in excess before starting every run.

Table I. Physical Properties of Solvents

	lit. (*19*, *20*)			obsd		
solvent	bp, °C	sp gr at 30 °C	RI[a] at 30 °C	bp, °C	sp gr at 30 °C	RI[a] at 30 °C
acetone	56.1	0.7790	1.3536	56.2	0.7780	1.3539
methanol	64.5	0.7825	1.3262	64.6	0.7821	1.3260
benzene	80.1	0.8684	1.4952	80.1	0.8681	1.4875

[a] RI = refractive index.

The components purified by fractional distillation were used in the work. The physical properties of these components measured at 30 °C are shown compared with the corresponding literature values (*19*, *20*) in Table I. These chemicals were supplied by B.D.H. (Ltd.), Bombay, and Sarabhai Merck Ltd., Bombay. The salts used in this work were of AnalaR/laboratory grade and supplied by Sarabhai Merck Chemicals and B.D.H. (Ltd.), Bombay. The performance of the equilibrium still for the determination of data in the presence of dissolved salts was earlier assessed by studying the system cyclohexane–carbon tetrachloride–ammonium sulfate. The data thus obtained compared well with the reported data (*15*) for this system.

Presentation and Discussion of the Results

The experimental data in the presence of salts are shown in Tables II and III and plotted as *x*–*y* and *t*–*x*–*y* diagrams with the compositions expressed on a salt-free basis in Figures 1–4. The reported *y*–*x* data for the two systems without salt (*8*) are also shown in respective figures. Besides these, the figures

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